Dear Participant

We are pleased to welcome you to the conference “Macromolecules in Constrained Environments”. The aim of this conference is to bring together researchers from different origins (academic and industrial) and different disciplines (chemistry, physical-chemistry, physics, etc.) in order to address the question of the physics of polymers and colloids in confined environments.

The field of physics in confined environments is a multidisciplinary field in deep adherence with industrial interests: oil field extraction, nanostructured and heterogeneous polymer blends, reinforcement of rubbers, etc. It is also a field where the recent academic development, both theoretical and experimental, is on the verge of important breakthroughs. Understanding the microscopic behavior of these systems in both processing/structure and structure/properties relationships is of utmost importance. The meeting will address this question using experimental, theoretical, and numerical approaches. During the five days of the meeting a significant portion of the time will be devoted to informal discussions and face to face conversations between participants especially during the three “open sessions”.

We hope that you will enjoy the conference and have a good time in the French Alps and at the “École de Physique des Houches”.

The Steering Committee.
Participants

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- Anne Goldberg (Solvay Nanotechnology Platform Project Leader)
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The conference is organized and partially sponsored by SOLVAY, an international chemical group, firmly committed to sustainable development and focused on innovation and operational excellence. Solvay assists industry in finding and implementing ever more responsible and value-creating solutions. The Group serves diversified markets, generating 90% of its turnover in activities where it is one of the top three worldwide. The Group is headquartered in Brussels, employs about 29,000 people in 55 countries and generated 12.4 billion euros in net sales in 2012.
DAILY PROGRAM
Monday, March 25th

- **8H45 – 9H15**
  - **INTRODUCTION**

- **9H15 – 10H40**
  - **PLENARY LECTURE**
    - Alexander Grosberg
    - “DNA and other biopolymers under confinement”

- **10H40 – 11H**
  - **COFFEE BREAK**

- **11H – 11H30**
  - **TALK**
    - Dina Osmanovic
    - “Unraveling the nuclear pore complex”

- **11H30 – 12H**
  - **TALK**
    - Vladimir Baulin
    - “Macromolecules constrained in lipid bilayers modify their structure and mechanical properties”

- **12H – 12H30**
  - **TALK**
    - Remy Kusters
    - “Barriers in the brain: Curvature and confinement as barrier for lateral diffusion on crowded membranes”

- **12H30 – 17H**
  - **LUNCH AND FREE TIME**

- **17H – 18H**
  - **INVITED TALK**
    - Luca Cipelletti
    - “Structure and plasticity of a block copolymer-nanoparticle composite”

- **18H – 18H30**
  - **TALK**
    - Roberto Perez-Aparicio
    - “Discriminating Reinforcement and Strain Amplification Effects in Reinforced Natural Rubber Elastomers”

- **18H30 – 19H30**
  - **RECEPTION**

- **19H30 – 20H30**
  - **DINNER**

- **20H30 – 21H30**
  - **OPEN SESSION**
Daily program

Tuesday, March 26th

- **8H45 – 10H10**
  - PLENARY LECTURE
  - David A. Weitz
  - “Highly constrained flow with microfluidics”

- **10H10 – 10H40**
  - TALK
  - Thomas Gibaud
  - “Interplay between chirality and geometrical constrains in colloidal membranes”

- **10H40 – 11H**
  - COFFEE BREAK

- **11H – 11H30**
  - TALK
  - Olivier Pierre Louis
  - “Giant slip at liquid-liquid interfaces using colloidal hydrophobic ball bearings”

- **11H30 – 12H**
  - TALK
  - Ye Xu
  - “Tuning Interactions and Shape of Macromolecules for Industrial Applications: An Overview of the Complex Assemblies of Soft Matter Laboratory”

- **12H – 12H30**
  - TALK
  - Larry Hough
  - “Tuning Interactions and Shape of Macromolecules for Industrial Applications: An Overview of the Complex Assemblies of Soft Matter Laboratory”

- **12H30 – 17H**
  - LUNCH AND FREE TIME

- **17H – 18H**
  - INVITED TALK
  - Doros Theodorou
  - “Multiscale Simulations of Macromolecular Conformation and Dynamics in Polymer-Matrix Nanocomposites”

- **18H – 18H30**
  - TALK
  - Anne-Caroline Genix
  - “Structure of Highly loaded Polymer-Silica Nanocomposites”

- **18H30 – 21H30**
  - SPECIAL EVENT
Wednesday, March 27th

- **8H45 – 10H10**
  - **PLENARY LECTURE**
  - Juan Colmenero
  - “Chain Dynamics in Asymmetric Polymer: experimental facts, MD-simulations and a theoretical approach based on the GLE formalism”

- **10H10 – 10H40**
  - **TALK**
  - Peiluo Shi
  - “Glass Transition Distribution in Miscible Polymer Blends: from Calorimetry to Rheology”

- **10H40 – 11H**
  - **COFFEE BREAK**

- **11H – 12H**
  - **INVITED TALK**
  - Margarita Krutyeva
  - “Dynamics of Polymer Chains Under Confinement in Alumina Pores”

- **12H – 12H30**
  - **TALK**
  - Wolfgang Paul
  - “Phase behavior of confined melts of semi-flexible polymers: a Monte Carlo study”

- **12H30 – 17H**
  - **LUNCH AND FREE TIME**

- **17H – 18H**
  - **INVITED TALK**
  - François Lequeux
  - “Understanding the dynamics of confined polymer in filled elastomers”

- **18H – 18H30**
  - **TALK**
  - Friedrich Kremer
  - “Molecular dynamics in 1- and 2-dimensional nanometric confinement as studied by Broadband Dielectric Spectroscopy”

- **18H30 – 19H30**
  - **POSTER SESSION**

- **19H30 – 20H30**
  - **DINNER**

- **20H30 – 21H30**
  - **OPEN SESSION**
Thursday, March 28th

- **8H45 – 10H10**
  - **PLENARY LECTURE**
  - Wilson Poon
  - “Jamming and the glass transition: same, different, or related?”

- **10H10 – 10H40**
  - **TALK**
  - Amandine Cuenca
  - “Sub-micron flow of polymer solutions”

- **10H40 – 11H**
  - **COFFEE BREAK**

- **11H – 11H30**
  - **TALK**
  - Olga Smerdova
  - “Towards an understanding of the role of polydispersity in oriented polymers: a SANS study of molecular orientation in homopolymer bimodal blends”

- **11H30 – 12H**
  - **TALK**
  - Cédric Lorthioir
  - “Segmental dynamics of interfacial polymer chains in nanocomposite hydrogels: from the nanosecond to the millisecond time scale”

- **12H – 12H30**
  - **TALK**
  - Yaha Rharbi
  - “The collective dynamics in block copolymer micelles at equilibrium”

- **12H30 – 17H**
  - **LUNCH AND FREE TIME**

- **17H – 18H**
  - **INVITED TALK**
  - Sharon Glotzer
  - “Crowded Colloids”

- **18H – 18H30**
  - **TALK**
  - Arantxa Arbe
  - “Structural and dynamical properties of ‘comb-like’ polymers”

- **18H30 – 19H30**
  - **OPEN SESSION**

- **19H30 – 21H30**
  - **DINNER**
Daily program

Friday, March 29th

- **8H45 – 10H10**  
  **PLENARY LECTURE**  
  Mark Ediger  
  “Molecular motion in polymer thin films and at the surface of molecular glassformers”

- **10H10 – 10H40**  
  **TALK**  
  Alain Dequidt  
  “Mechanical Properties of thin confined Polymer films close to the glass transition in the linear regime of deformation: theory and simulations”

- **10H40 – 11H**  
  **COFFEE BREAK**

- **11H – 11H30**  
  **TALK**  
  Alexey V. Lyulin  
  “Competitive effects in the dynamics of polymer nanocomposites”

- **11H30 – 12H30**  
  **CONCLUSION**

- **12H30 – 13H30**  
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| The dynamic and the glass transition of polystyrene in nanoparticules: the analogy with thin films (erratum) | Y. Rharbi, L. Porcar, F. Boué, Q. Nawaz, 1 M. Yousfi                        | Laboratoire de Rhéologie et procédés, UJF/INPG/CNRS, Grenoble, France  
Institut Laué-Langevin, Grenoble, France  
Laboratoire Léon Brillouin, CEA Saclay Gif-sur-Yvettes, France |
| Crowded Colloids                                                     | Sharon Glotzer                                                            | Laboratory for Computational Nanoscience and Soft Matter Simulation  
University of Michigan                                                   |
| Structural and dynamical properties of ‘comb-like’ polymers          | Arantxa Arbe                                                              | Centro de Fisica de Materiales CSIC-UPV/EHU, Spain                          |
| Molecular motion in polymer thin films and at the surface of molecular glassformers | Mark Ediger                                                               | Department of Chemistry, University of Wisconsin-Madison                   |
| Mechanical Properties of thin confined Polymer films close to the glass transition in the linear regime of deformation: theory and simulations | Alain Dequidt, Didier R. Long, Paul Sotta and Olivier Sanseau            | Institut de Chimie de Clermont-Ferrand  
Laboratoire des Polymères et Matériaux avancé – CNRS/Solvay, Sains Fons, France |
| Competitive effects in the dynamics of polymer nanocomposites        | Alexey V. Lyulin, C. Batistakis, M.A.J. Michels                           | Department of applied physics, Technische Universiteit Eindhoven             |
DNA is so long that spatial confinement is a natural situation for it in most biological systems, while understanding its physics is rather different depending on the scale. For viruses, the confinement is very tight; for bacteria, it is much less tight; and for higher cells it acquires a new quality related to DNA topology. On every scale, there is some understanding of the relevant physics, but there are also exciting open questions. Time permitting, other biopolymer systems can be also discussed, such as RNA with its rearrangement of secondary structure upon confinement.
Unraveling the Nuclear Pore Complex

Dino Osmanovic, Ian Ford, Bart Hoogenboom
London Centre for Nanotechnology

Physically interesting behavior can arise when soft matter is confined to nanoscale dimensions. A highly relevant biological example of such a phenomenon is the Nuclear Pore Complex (NPC) found perforating the Nuclear Envelope of all eukaryotic cells. In the central conduit of the NPC of 50–60 nm diameter, a disordered network of proteins regulates all macromolecular transport between the nucleus and the cytoplasm. Its selectivity for larger macromolecules relies on changes in a permeability barrier that is formed by these unstructured proteins, induced by interactions of these proteins with so-called importins and exportins. The exact mechanism by which this works is unknown. We have modeled the NPC as a polymer-coated pore via classical Density Functional Theory (DFT) and Monte Carlo (MC) approaches, to show that — for physiologically relevant parameters — the pore can act as a bi-stable switch, in which small changes in polymer-polymer interaction causes the system to switch between a closed, centrally condensed state and an open state in which the polymers condense at the pore wall. We have mapped this behavior in a phase diagram and will present results for indentation curves, transport rates and possible effects of different macromolecules, which will allow direct comparison to experiment.

Figure 1: Evolution of combined polymer-Importin structure for parameters and chemical potentials
Macromolecules constrained in lipid bilayers modify their structure and mechanical properties

Vladimir Baulin¹, Sergey Pogodin², Yachong Guo¹
1. Departament d'Enginyeria Química, Universitat Rovira i Virgili, Tarragona, Spain
2. ICIQ, Tarragona, Spain

Double layers self-assembled from lipid molecules represent a confined geometry for molecules interacting with bilayers and consist of alternating hydrophilic and hydrophobic parts. The resulting structure and the dimensions of the bilayers are irrevocably fixed by the molecular structure of lipids. Proteins, antimicrobial peptides, disordered-protein aggregates, drug-delivery polymers confined in the bilayers can modify the structure and properties of the bilayers.

In turn, the bilayer structure imposes severe restrictions on the molecular structure of these membrane active biomolecules. As these molecules move from solution to membrane-bound states there are dramatic changes in their structure and/or aggregation due to the two different chemical environments. After binding further changes may occur, such as re-organization.

![Image of proteins in different states](image)

Fig. 1. Upon stress conditions cells express LEA proteins, which self-assemble into rigid helixes. These proteins are membrane active and are able to modify the properties of the membranes.

Late embryogenesis abundant (LEA) proteins are an example of such molecules. These proteins are expressed in plant and some animal cells in response to desiccation conditions, and they increase the ability of such cells to withstand desiccation stress. To gain insight into the thermodynamics of membrane association, we model the resulting R-helical structures (Fig. 1) as infinite rigid cylinders patterned with hydrophobic and hydrophilic stripes oriented parallel to their axis¹. Using the Single Chain Mean Field (SCMF) theory that directly gives equilibrium structures of molecules in solution and in the membrane²,³, we have shown¹ that a regular surface patterning of LEA proteins may facilitate membrane association and controls the depth of the equilibrium their penetration into the bilayer.

SCMF theory can give detailed information about the structure and physical properties (e.g., compressibility) of lipid membranes when interacting with biological macromolecules that can be difficult to achieve in direct experiments. Computer simulations can also reveal the molecular mechanisms of these interactions, and the conformational changes that biomolecules undergo while transferring from water to the quasi two-dimensional geometry of the membrane.

On the example of interaction of hydrophobic homopolymers and block copolymers with lipid bilayers we demonstrate the structural changes in the bilayers induced by the presence of the
polymers of different composition. Rearrangements of hydrophobic and hydrophilic regions due to polymers result in volume fractions of components and significant changes in the elasticity of the bilayers.

Fig. 2. Structural changes in the lipid bilayer upon addition of hydrophobic polymer T8 into the lipid bilayer. The concentration of the polymer (green) is increased from left to right. Hydrophobic tails (blue) and hydrophilic heads (red) rearrange in order to accommodate the polymer.

This microscopic information can be validated against neutron and X-ray scattering and will elucidate the fundamental mechanisms of membrane activity and selectivity of biomolecules and the key parameters that control self-assembled membrane structures.

References:
Barriers in the brain: Curvature and confinement as barrier for lateral diffusion on crowded membranes

Remy Kusters, Cornelis Storm
Faculteit Technische Natuurkunde, Technische Universiteit Eindhoven, Postbus 513, 5600 MB Eindhoven, Netherlands

Figure 1: The experimentally observed shapes of the dendritic spines are directly linked to their neurological functionality (Bourne et al. [1]). The morphology of the spine and, more specifically, the radius of the neck dramatically increases the characteristic escape time of receptors for decreasing neck radius.

The neural system uses chemical and electrical signals to transfer and store information within the brain. A single neuron is composed of a cell body, from which several dendritic arms and one axonal arm emerge. Electrical signals are processed via an axon and chemically transported via the synapse to a neighboring dendrite of another neuron. In the adult brain, the structural changes of these connections by means of structural plasticity, formation and elimination are thought to underlie aspects of learning and memory [2, 3, 4]. I will show in this talk how morphology and curvature of the membrane surrounding the dendritic spine influences the functionality of the synapse.

The receptor molecules which are crucial for the process of learning and memory are the excitatory glutamate receptor called NMDA and a glutamate receptor, called AMPA. The combination of these receptor molecules enable a neuron to respond to a stimulus the next time it occurs. To keep the receptors in the spine domain, the spine has various mechanisms to suppress the diffusion of these receptors. Roughly, three different types of structures are reported in experiments: small stubby spines, thin filopodia-like protrusions called thin spines and spines with a bulbous head called mushroom spines. One of the main mechanisms underlying learning and memory, called LTP (long-term potentiation), causes enlargement of the head of the spine [1, 3]. This suggests that the shape and morphology of the head plays an important role in the functionality of the synapse and that large dendritic heads have an increased neurological functionality. The PSD (Post Synaptic Density) situated on the top of the dendritic spine has been shown to contain proteins relevant for the signal transport from the synapse to the axon [Holtmaat 2009], most notably an increased density of AMPA receptors [1, 3, 4].
The endo- and exocytosis of AMPA together with the lateral surface diffusion of receptors are thought to be the general mechanisms accounting for local changes in receptor density on the surface of spines [5]. In this talk the timescales I will demonstrate that over which particles diffuse out of the spine are strongly influenced by the morphology and curvature of the dendritic spine. More specifically, I will show how the radius of the neck dramatically influences the diffusion of the receptors (see figure 1) and thus show that morphology and curvature serve as a mechanism for confining membrane bound particles to the dendritic spine.

This diffusion problem is addressed numerically and analytically. Numerically, the diffusion of these receptors is simulated with a Brownian Dynamics simulation of interacting particles on the surface of a curved membrane. Analytically, we characterize confinement with the Mean First Passage Time (MFPT) for a particle escaping through the boundary of a surface. Both the numerical and analytical results show that for a spine-like structure the diffusion of the receptors is increasingly hindered for decreasing neck size of the spine. Besides the geometrical effects, our numerical simulation provides novel insights in crowding and jamming effects for interacting particles on curved surfaces. Both these geometrical and crowding effects increase the relevant time scale over which lateral diffusion can occur, greatly suppressing the escape rate. This makes it possible to confine receptors to their functional domain over very long timescales.

References:
Structure and plasticity of a block copolymer-nanoparticle composite

E. Tamborini, N. Ghofraniha, J. Oberdisse, L. Ramos, L. Cipelletti
L2C UMR 5221 Université Montpellier 2 and CNRS

We use confocal microscopy, rheology and light scattering to investigate the structure and the plasticity of a composite material, formed by Pluronics F108, a commercial triblock copolymer to which small amounts of colloidal nanoparticles are added. At sufficiently high polymer concentration and temperature, the block copolymer forms micelles that are regularly arranged on a FCC lattice, while the nanoparticles are preferentially segregated in the grain boundaries between micelle crystallites. We show that both the segregation efficiency and the grain size can be tuned by varying the speed at which the sample is solidified and the nanoparticle amount. We rationalize our findings by extending classical theories for nucleation and growth of crystals to account for the presence of the nanoparticles.

We moreover investigate material fatigue and plasticity by measuring microscopic rearrangements in our composite material submitted to thousands of deformation cycles. Light scattering data collected at several scattering vectors and for various deformation amplitudes can be scaled onto a single master curve, exhibiting two regimes. In the first regime, the shear-induced dynamics become increasingly slower with time ("aging"), while a stationary regime where plasticity does not evolve anymore is eventually reached. Remarkably, the cross-over between the aging and the stationary regime depends on the probed length scale, larger length scales reaching the stationary state earlier. We propose a simple physical picture to rationalize these results.
Discriminating Reinforcement and Strain Amplification Effects in Reinforced Natural Rubber Elastomers

Roberto Pérez-Aparicio¹, Arnaud Vieyres¹, Pierre-Antoine Albouy², Olivier Sanseau¹, Didier R. Long¹, and Paul Sotta¹

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During last decades, several mechanisms have been proposed to explain the remarkable mechanical properties of reinforced elastomers with nanometric particles or aggregates, and the complexity of their structure and dynamics has been evidenced through many experimental techniques (dielectric and mechanical spectroscopy, NMR, etc.). Understanding the various mechanisms associated to reinforcement implies combining techniques which give access to complementary information. Here, we propose an experimental approach based on the combination of different techniques in order to discriminate reinforcement and strain amplification effects in natural rubber elastomers filled with carbon black or silica.


In unfilled materials, all measurements are nicely correlated, which is in agreement with rubber elasticity theory [A. Vieyres, et al., Macromolecules 46, 889 (2013)]. In filled materials, results of different techniques refer to various parts of the material. Thus, analyzing the deviations with respect to the behavior of the pure unfilled elastomer matrix allows discriminating various physical mechanisms. In particular, it is observed that the mechanical response at medium/large strain amplitudes is well correlated to other measurements, taking into account, however, strain amplification effects (which amplify chain segment orientation under stretching). On the other hand, mechanical reinforcement effects observed in the linear regime (at small strain amplitude) are not correlated to the properties of the elastomer matrix.
Highly constrained flow with microfluidics

David A. Weitz
School of Engineering and Applied Sciences/Department of Physics
Harvard University, Cambridge, MA 02138

The physical constraints on flow that can be achieved with microfluidic devices provides opportunities to investigate flow phenomena in highly controllable geometries, and to use these physical constraints both to discover new flow properties and to create new types of materials. This talk will provide an overview of developments in both directions. It will discuss the use of microfluidic systems as models for flow in porous materials, and will explore the new insights that can be obtained by combining these models with modern imaging methods. In addition, the talk will explore the creation of new types of materials by constraining and controlling the flow of fluids, both liquid and gas.
Interplay between chirality and geometrical constrains in colloidal membranes

Thomas Gibaud
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The interfacial tension between molecular species in self-assembling systems plays a crucial role in determining the physical properties of the mesoscopic assemblages. The predominant method for controlling interfacial tension is the addition of surfactant molecules, which preferentially adsorb onto the interface and modify the interactions between the two phases. Using a model colloidal membrane (Fig.1) composed of chiral, rod-like fd-viruses, I will present a new method for controlling interfacial tension which does not require additional surfactant components, but instead utilizes the intrinsic chirality of the constituent rods.

I will demonstrate that chirality can be used to continuously tune the interfacial tension of a membrane and to drive a dramatic phase transition from two-dimensional membranes to one-dimensional twisted ribbons. Using a wide variety of microscopic techniques, this transition is characterized over length-scales, ranging from nanometers to microns. Then, using optical forces we demonstrate that malleable chiral assemblages can easily be moved, stretched, attached to each other, and transformed between multiple polymorphic states, thus enabling precise assembly and sculpting of highly adaptable materials with complex topologies. Finally we show that the interplay between geometrical constrains and chirality lead to two types of new defects, Fig.2

Fig.1 using a mixture of fd viruses as model colloidal rods and polymers we induce the condensation of the rods into colloidal membranes, a monolayer of aligned rods. The microscopy images show from left to right the transition from colloidal membranes to twisted ribbons as we increase the chirality of the rods. The schematics below illustrate the structure of the membrane and the twisted ribbon.
Fig. 2 Left: as chiral membranes with opposite chirality coalesce they form point defect. Right: as chiral membranes with identical chirality coalesce they form p-all defects.

References:
Giant slip at liquid-liquid interfaces using colloidal hydrophobic ball bearings

Q. Ehrlinger, L. Joly, O. Pierre-Louis
ILM, Lyon 1, France

While slip in structured liquid-solid interfaces has been subject to a number of studies, there has been to our knowledge no study of the slip behavior of structured liquid-liquid interfaces. We show that liquid-gas-liquid interfaces stabilized by hydrophobic spherical colloids behave as ball bearings under shear and exhibit giant slip. Using a scaling analysis and Molecular Dynamics simulations we predict that, when the contact angle $\theta$ between the colloids and the liquid is large, the liquid-liquid slip length is independent on the liquid viscosity and diverges as $R^3(\pi-\theta)^{-3}$ where $R$ is the bead radius, and $\rho$ is the bead density. This system may lead to slip lengths approaching the millimeter scale.

Figure 1: Molecular Dynamics simulation of a periodic array of beads.

Reference:
Tuning Interactions and Shape of Macromolecules for Industrial Applications: An Overview of the Complex Assemblies of Soft Matter Laboratory

Larry Hough\textsuperscript{1}, Ryan J. Murphy\textsuperscript{1}, Ahmed Alsayed\textsuperscript{1}, Chantal Badre\textsuperscript{1}, Pascal Herv\textsuperscript{1}, Ye Xu\textsuperscript{1,2}, Tim Still\textsuperscript{2}, Arjun Yodh\textsuperscript{2}.

1. Complex Assemblies of Soft Matter, Solvay, Bristol, PA, USA
2. University of Pennsylvania, Philadelphia,

The Complex Assemblies of Soft Matter Laboratory (COMPASS UMI 3254) is a joint laboratory between Solvay, The University of Pennsylvania, and Le Centre national de la Recherche Scientifique (CNRS: The French National Research Center). The COMPASS is a unique collaboration bringing together academic, industry and research partners with an expertise in the creation, manipulation and understanding of soft matter. This will be an overview of ongoing work in COMPASS that focuses on the modern applications of macromolecules in constrained environments. Specifically, we will discuss two topics, the versatility of macromolecules in industry due to tuning of the interactions and assembly, and the use of shape to obtain new properties. In the first section, we will discuss the confinement of temperature sensitive microgels to obtain thermo-rheological behavior useful in oil field applications. In addition, we will discuss the confinement of surfactants into multilamellar vesicle phases and their uses in rinse off personal care formulations. Interesting, both of these soft systems demonstrate jamming behavior, and the striking similarities between the systems will be discussed. In this section, we will also discuss the characteristics of conducting nanogels confined in film as a replacement for Indium Tin Oxide in electronic devices. In the second section, we will discuss how anisotropy can be used to bring about new materials properties for applications. Specifically, the use of ellipsoidal colloids confined within droplet to aid in homogeneous drying of paints, inks, coatings and films.
Multiscale Simulations of Macromolecular Conformation and Dynamics in Polymer-Matrix Nanocomposites

Georgios G. Vogiatzis and Doros N. Theodorou
National Technical University of Athens, Athens, Greece.

The mechanical and rheological properties of a polymer-matrix nanocomposite may depart dramatically from those of the pure matrix. The quantitative relationships between composition and size of polymer chains and nanoparticles, processing conditions, degree of dispersion of the nanoparticles, dynamics of the matrix chains, and macroscopic properties are still elusive. Molecular simulation holds great promise as a means for understanding and predicting these relationships, but faces serious challenges associated with the broad spectra of length and time scales governing nanocomposite properties.

We are developing a multiscale simulation strategy designed for materials consisting of nanoparticles of roughly spherical shape within amorphous polymer matrices. This strategy encompasses atomistic molecular dynamics (MD), coarse-grained connectivity-altering Monte Carlo (MC), Field Theory- inspired Monte Carlo (FTiMC), and entanglement network modeling. Each level of representation invokes parameters that can be extracted from the previous (more detailed) level, such that all predictions are ultimately based on an atomistic force field.

Atomistic MD simulations are useful in elucidating the details of molecular packing near nanoparticle surfaces and in quantifying how segmental dynamics is affected by the presence of nanoparticles. As the time scales addressed by MD (up to 100 ns in our simulations) are very short in comparison to the longest relaxation times of the long-chain systems we study, coarse-grained MC simulations are of strategic importance in achieving equilibration at all length scales. By developing coarse-grained effective potentials from detailed atomistic ones via the Iterative Boltzmann Inversion method, rigorous MC sampling of the coarse-grained models with connectivity-altering algorithms, and reverse- mapping back to the atomistic level, one can generate well-equilibrated atomistic configurations to study structure and dynamics. We have applied this strategy to quantify the effects of incorporating fullerenes on the segmental motion and the glass transition of long-chain atactic polystyrene.

In the FTiMC approach polymer chains are represented as freely jointed sequences of Kuhn segments, and nanoparticles as single spherical entities. Polymer non-bonded interactions are taken into account via a functional of local density, while nanoparticle-polymer and nanoparticle-nanoparticle interactions are represented via integrated atomistic potentials. This approach is particularly useful for studying large (~100 nm) systems containing many nanoparticles, to elucidate changes in the conformation and spatial extent of polymer chains resulting from the presence of the nanoparticles. We have applied FTiMC to nanocomposites consisting of tightly crosslinked 3.6 nm-radius polystyrene (PS) nanoparticles within molten linear PS matrices of various molar masses, studied experimentally with Small Angle Neutron Scattering (SANS) by Mackay and coworkers. Our simulation results reveal swelling of the polymer melt coils with increasing nanoparticle volume fraction, in good agreement with SANS. FTiMC has also been applied to systems consisting of silica nanoparticles dispersed in monodisperse atactic PS. The nanoparticles are either bare or carry monodisperse surface-grafted PS chains of variable molar mass at various grafting densities. Predicted scattering curves from the grafted polymer corona are validated against detailed SANS investigations carried out by Chevigny et al.
Structure of highly loaded Polymer-Silica Nanocomposites

A-C Genix¹, G.P. Baeza¹, M. Tatou¹, M. Couty², J. Oberdisse¹
1. Laboratoire Charles Coulomb, Université Montpellier 2, Montpellier, France
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The mechanical reinforcement of polymer matrices by nanoparticles is a fundamental problem with far reaching applications, e.g., for car tires. From a conceptual point of view, it is generally recognized that the filler structure has a strong impact on the mechanical properties, accompanied by the effect of chain structure evolving in the hard filler environment, and the filler-chain interactions. All these contributions are related to the filler structure, and it is thus important to be able to characterize it in detail.

In this work, the structure of SBR-silica nanocomposites designed to reproduce key features of industrial samples, but of simplified composition, has been studied on length scales extending from the nanometric primary particles to microns. We propose an original method for scattering data analysis of such multi-scale systems by including self-consistent polydisperse form and structure factors of aggregates.[1] The complex structure of the silica within the nanocomposites will be quantitatively modeled in a step-by-step manner, starting with the primary silica beads as basic building units (10 – 20 nm range). These beads are found to be aggregated in small clusters, the typical radius of which (40 nm range) will be determined by Kratky plots. These aggregates are themselves concentrated in large-scale fractal branches (thickness ca. 150 nm, extending over microns). Inside these branches, the small aggregates repel each other. Within our model, this is described with a hard-sphere excluded volume interaction potential, which induces a characteristic depression of the scattered intensity at intermediate angles (Figure 1). This depression is directly related to the local concentration of aggregates, which is higher than the nominal silica volume fraction due to the confinement in the fractal branches, and the presence of polymer inside the aggregates. Therefore, a quantitative TEM analysis was used to estimate the volume fraction of fractal branches.

Figure 1: Silica structure of nanocomposites. a) Reduced scattered intensity I(q)/Ωsi measured by SAXS for a series of silica volume fractions (8.4–21.1% vol.). Dotted line: form factor of the silica beads. b) TEM pictures.
Secondly, we have set up an independent Monte Carlo simulation in order to calculate the low-q limit of the polydisperse inter-aggregate structure factor, which quantifies the depression. Using a polydisperse aggregate form factor obeying the same polydispersity, the mass of the small aggregates (or, equivalently, their internal silica volume fraction, here called compacity) and their concentration inside the fractal branches can be extracted from the scattered intensity. In parallel, the rheological properties of these silica structures in the SBR-matrix are characterized with oscillatory shear. The resulting reinforcement curve of the high-frequency storage modulus can be described using a combination of hydrodynamic reinforcement for silica fraction below a critical percolation fraction, and a percolation law above. It is interesting to note that the aggregate compacity obtained from the structural analysis (SAXS and TEM) is fully compatible with the reinforcement data.

On the other hand, for future work, it may be important to be able to compare the results obtained here to model systems where the filler is a well-defined nanoparticle. In this case, we were able to follow the chain conformation in hard filler environments using contrast-variation small angle neutron scattering (SANS). In polyacrylate latex based nanocomposites where the silica structure is well characterized, it has been found that the radius of gyration is not disturbed by the silica loading in a given state of aggregation (typically ten primary silica particles per aggregate, percolating at high concentration).[2] This important result opens the way for a systematic study of the chain structure in complex environments.

References:
Chain Dynamics in Asymmetric Polymer Blends: experimental facts, MD- simulations and a theoretical approach based on the GLE formalism

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Miscible polymer blends are systems of wide technological interest whose dynamical and rheological properties can be tuned by varying the mixture composition. They are also very interesting systems from a basic scientific point of view. Even being miscible, these systems are dynamically heterogeneous: starting from two homopolymers with different mobility (different glass transition temperatures Tg) two separated segmental (ά) relaxations are still observed in the miscible blend state. When the difference in segmental mobility (Tg) of the two-homopolymer components is not too high, they exhibit qualitative similar dynamic features in the blend. However, a rather different scenario emerges for low concentration of the fast component, if the two homopolymers display very different Tg’s. In this case, the two components in the blend exhibit strong dynamic immiscibility, with a large separation (dynamic asymmetry) in their respective ά-relaxation times. In such conditions the motion of the fast component seems to be strongly restricted (“confined”) by the slowly relaxing matrix formed by the slow component.

Recently, we have extended the investigations of dynamic properties of asymmetric polymer blends to the large-scale dynamics (chain dynamics), which drives rheology and processing of polymer systems. We have mainly used dielectric spectroscopy [1] neutron scattering [2] and molecular dynamics (MD) simulations [3]. We found that the anomalous dynamic features induced by the slow matrix on the fast component also extend to this large-scale regime. The dynamic asymmetry induces strong non-exponentiality of the Rouse modes for the fast component. Moreover, we observe a striking crossover, by increasing the dynamic asymmetry in the blend, to a regime resembling scaling features characteristic of entangled- like chain dynamics, despite the used chain length being much shorter than the critical value for entanglement. We associate these features to strong memory effects that are induced by

the slow nature of the confining matrix and which breaks one of the main assumptions of the Rouse model: the un-correlation of the external forces acting on the tagged chain. Theoretical methods based on the generalized Langevin equation (GLE) formalism seem to be a suitable framework to describe chain dynamics in asymmetric polymer blends [4]. In this framework, a direct and nontrivial correlation between the parameter giving the wavelength scaling of the Rouse relaxation times and the non-exponential parameter of the corresponding Rouse mode correlators can be deduced [4, 5]. This correlation, which is nicely corroborated by MD simulation results, is the key to calculate GLE expressions for the physical magnitudes controlling chain dynamics as, for instance, incoherent neutron scattering function of a polymer segment and normal-mode relaxation (“end-to-end fluctuations”) observed by dielectric spectroscopy [5].
In this lecture we will give an overview of the “state of the art” on this topic, including examples from both experimental techniques and molecular dynamics (MD) simulation.

References:
Glass Transition Distribution in Miscible Polymer Blends: from Calorimetry to Rheology

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At their glass transition, simple liquids and polymers exhibit a large spectrum of relaxation - with a width of more than 4 decades in time. Blends of miscible polymers exhibit even larger relaxation spectrum. Here, we assume that a blend can be considered as an ensemble of domains of various local glass transition temperatures. Using calorimetric data, with or without aging, we probe the distribution of glass transition temperature (T\textsubscript{g}) of miscible polymer blends of PB/SBR. Using self-consistent averaging method inspired by the Olroyd- Palierne model, we predict quantitatively, with no adjustable parameter, the viscoelastic spectrum of our blends from the T\textsubscript{g} distribution obtained by calorimetry. This quantitative prediction confirms thus the assumption that mechanically, a blend can be considered as an ensemble of domains each of which having a different glass transition temperature.
Dynamics of Polymer Chains Under Confinement
In Alumina Pores

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Understanding the structure and dynamics of polymers close to the confining solid surface (interface) and in the intermediate phase between the interface and a bulk phase (interphase) is important for applications in nanotechnology such as coatings for electrical devices, lubricants, and polymer nanocomposite materials. Confinement effects in polymer melts may lead to unusual properties. This concerns both the chain conformation, which may be distorted in particular if the chain dimensions are significantly larger than the confinement size, as well as chain dynamics, which may be altered due to surface interactions and changes of topology and chain self-density.

In this talk I will focus on the influence of the solid surfaces and their interaction with polymers on the dynamics of polymer melt by neutron scattering. The confining systems are presented by well-ordered cylindrical Alumina nanopores (2D confinement). The segmental dynamics on the local time scale is studied by quasielastic neutron scattering (QENS) up to a few nanoseconds and on the large scale dynamics measured by high resolved neutron spin-echo (NSE) spectroscopy extending the time scale to a few hundred of nanoseconds [2]. The main goal is investigation of the influence of the confining surfaces and geometrical confinement on the structure and dynamics of polymer chains at the interface and their extent into a possible interphase for different types of interaction between solid walls and the melt. In particular, we will study the influence of the surface on the local segmental dynamics, unentangled Rouse dynamics and the polymer entanglement network [3,4,5].

References:
Towards an understanding of the role of polydispersity in oriented polymers: a SANS study of molecular orientation in homopolymer bimodal blends

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Although molecular orientation is essential in polymer film and fiber drawing processes, it can also be an undesirable consequence of injection molding and extrusion. Many properties of such processed thermoplastics depend on the degree of orientation, which in turn depends on the polymer’s molar mass distribution and on the processing conditions and flow history. The focus of our Nottingham laboratory over the last few years has been to develop fully predictive physical models for solid-state properties of processed polymer glasses, by combining constitutive models for glassy behaviour in the solid state with molecularly-based models for the rheological response. Using this approach we have recently shown that quantitative predictions of optical birefringence, crazing stress and sub-Tg mechanical response are possible for the special case of oriented monodisperse linear amorphous polymers [1].

The focus has now shifted towards rendering this type of modelling more relevant to industrial homopolymers, but this requires an understanding of the rheology and solid-state properties of mixtures of interacting polymeric length scales. Hence, the present study encompasses an experimental study of such interactions between length scales in the simplified problem of a bimodal blend of monodisperse homopolymers. A special set of monodisperse polystyrene (PS) blends with 4:1 mass ratio of short to long chains (degrees of polymerisation (DoP) of ~900 and ~2100 respectively) was synthesised in Durham from carefully selected mixtures of hydrogenous and deuterated styrene monomers. Six blends with carefully matched ratios of DoP but purposefully varying levels of deuteration between length scales were produced. In order to reproduce the typical range of orientations observed in industrial processes, isotropic specimens from each blend were subjected to the same orientation conditions: uniaxial drawing to draw ratios ranging between 2 and 5 in an environmental chamber at temperatures ranging from Tg to Tg + 30 at constant nominal strain rate. Molecular orientation was frozen-in by immediate quenching of the specimens after stretching. Stresses were recorded during stretching.

Molecular orientation of the blends at a segmental level was quantified through measurements of optical birefringence, and is compared to that of a monodisperse PS with DoP ~2100 in Fig.1 for specimens stretched to constant draw ratio 3 at varying temperatures above Tg. The effect of the low molar mass component in the blend is to accelerate the average segmental relaxation relative to the monodisperse high molar mass PS, and the birefringence is lower at the higher draw temperatures.

In order to study molecular orientation over a wider range of length scales, neutron scattering experiments were carried out on oriented specimens from blends with varying levels of deuteration at the SANS II facility at the Paul Scherrer Institute. The purpose of this was to obtain information about orientation of the specific length scales within the bimodal blend, and to contribute to better understanding of mechanisms of chain retraction, reptation and constraint release when multiple length scales are present. Fig. 2 shows measured scattering intensities as a function of scattering
vector \( q \) for one of these oriented blends, stretched to draw ratios varying from 1 to 5, and hence in varying orientation states. Because of the presence of several molecular lengths, these scattering functions cannot be treated by standard methods [3], and are instead made up of the following components:

\[
I(q) = (b_h - b_d)^2 \left[ (1 - x_s)N_s z_s^2 P_s(q) + (1 - x_l)N_l z_l^2 P_l(q) + (1 - x_l)^2 N_l z_l^2 Q_{ll}(q) + 2(1 - x_s)(1 - x_l)N_s N_l Q_{ls}(q) \right]
\]

where \( P \) are intra-chain form factors and \( Q \) are inter-chain functions, \( b \) is the scattering length, \( x \) is the fraction of deuterated chains, \( N \) is the number of molecules, and \( z \) is the degree of polymerization. Short and long chains are designated by indices \( s \) and \( l \) respectively. A number of approaches are being considered in our laboratory to attempt for the first time to identify inter- and intra-chain functions, allowing the determination of molecular size and conformation (from the radii of gyration) for specific length scales within a bimodal blend.

This work will be employed to inform existing rheological models for bimodal blends as to the cross-length scale contributions. Eventually, the aim is to enable practical rheological predictive models for polydisperse commercial polymers, and for these models to be employed in full melt-to-solid product simulations of processed, oriented polymer parts.

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**Fig. 1.** Effect of draw temperature on birefringence of the bimodal blends. Also shown is data for monodisperse 262kDa PS from [2] for comparison.

**Fig. 2.** Scattering intensities as a function of draw ratio at fixed draw temperature, in the parallel direction to stretching in one of the six blends.

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References:
Understanding the dynamics of confined polymer in filled elastomers

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Since about 50 years, it has been noticed that the counter-intuitive mechanics of filled rubber is the signature of a specific dynamics of the polymer at the particles interface. However, after numerous discussions, it has been recognized that quantitative analysis of this confinement effect has required the design of model systems. We have since more than 10 years synthetized model filled elastomers: polyacrylates matrices embedding monodisperse spherical silica particles. We have combined on a long term study various techniques such as NMR, Neutrons scattering, calorimetry and mechanical analysis, to characterize precisely these confinement effects. We have nowadays a quite complete characterization of the effect of confinement of polymer by silica particles.

It appears that in first approximation, a Tg gradient model is able to capture some of the confinement effects like calorimetry. However, other effects -like the non-linearities for instance- are not capture by this model, and a broadening of the dynamics must be involved to explain them. I will however explain that all the confinement effects that we observe are consistent with the model of heterogenous dynamics of D. Long, and the recent simulations of his team.
Molecular dynamics in 1- and 2-dimensional nanometric confinement as studied by Broadband Dielectric Spectroscopy


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The (dynamic) glass transition of polymers in nanometer thin layers is both a prevailing but as well a highly controversial topic. In the current review the literature for the most studied case of polystyrene (as freestanding films or as deposited and suspended layers) will be discussed. Based on this, the extraordinary impact of sample preparation is immediately evident and outlined in detail. Recent results are presented on nanometric thin (≥5 nm) layers of polystyrene (PS) having widely varying molecular weights and polymethylmethacrylate (PMMA) deposited on different substrates. For the dielectric measurements two sample geometries are employed: the conventional technique using evaporated electrodes and a recently developed approach taking advantage of silica nanostructures as spacers. All applied methods deliver the concurring result that deviations from glassy dynamics and from the glass transition of the bulk never exceed margins of 3 K independent of the layer thickness, the molecular weight of the polymer under study and the underlying substrate. Novel experiments are described on thin layers of polyisoprene, a type A polymer, having relaxation processes on two different length scales, the segmental and the normal mode. A further exciting perspective is the measurement of the dynamics of isolated polymer coils, for which first results will be presented.

The question of how the dimensionality of geometrical confinement influences the molecular dynamics is up to now unexplored; 1-dimensional (1-D) confinement is realized in nanometer thin layers or films, while 2-D constraints take place for molecules contained in nanopores. Experimental results of poly-cis-1,4-isoprene (PI) in thin layers down to 6 nm thickness prepared as part of a nanostructured capacitor arrangement and when deposited in unidirectional nanopores having pore diameters down to 4 nm will be presented. Due to the fact that PI is a type – A polymer having two dielectrically active relaxation processes; one corresponding to the fluctuations of 2 – 3 polymer segments and the other being assigned to that of the end-to-end vector of the chain, it is possible to sense the dynamics at two well separated length scales. First results will be presented and compared to studies on the dynamics of low molecular weight glass formers and liquid-crystals confined in 2-D constraints of nanopores.

References:

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There is a large and growing literature on 'jamming and the glass transition' in soft materials. It is not always clear in this literature if, and if so how, the two phenomena are related; the situation is not helped by the use of the word 'jamming' to mean a multitude of things, not always with careful definition. In this lecture, I review recent work on the subject, and suggest that the two phenomena are distinct ends of a spectrum, with a fascinating continuum lying between them. The phenomenology in practice is further complicated by factors that are almost never entirely absent in experiments, such as sedimentation and polydispersity. Nevertheless, I suggest that a clear distinction is still possible in principle, and desirable in practical description.
Sub-micron flow of polymer solutions

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Rheology of high molecular weight polymer solutions at submicroscale is investigated, with a particular emphasis on the wall slip characterization. Our approach is to measure the velocity of a pressure-driven flow in sub-microchannels in order to determine an effective viscosity of fluids. We have been using fluorescence photobleaching as a non-invasive technique to evaluate the velocity of a pressure-driven flow in 175 to 4000 nm high channels. A striking reduction of the effective viscosity is observed with the confinement, as compared to the bulk one. Direct measurement of slip velocity in microchannels is performed, using z-resolved micro-Particle Image Velocimetry (PIV). This study enables to draw two important conclusions, which have never been experimentally demonstrated. Slippage of polymer solutions in the semi-dilute unentangled regime is greatly reduced by confinement. A distinction of bulk and surface phenomena seems no longer valid at the submicroscale. Besides, slippage is supposed to dominate the flow in nanoslits as the channel height becomes smaller than the slip length measured in microchannels. Thus, the effective viscosity drops when the channel height decreases. The viscosity reduction below 1 m is not as drastic as predicted by macroscopic slippage and bulk rheology, which attests of a reduction of both slip length and depletion layer thickness due to confinement. This result is interpreted in terms of migration, which seems to be cancelled in nanoslits, in agreement with some recent simulations. A distinction of bulk and surface phenomena seems no longer valid at the submicroscale. This experimental method is also adapted to the study of surfactant solutions flows at the submicroscale.

Fig. 1 Top view of a micro-nano glass chip and principle of a velocity measurement at submicroscale: a pressure driven flow is established in nanoslits and imaged after a photobleaching procedure. The temporal evolution of intensity profiles enable to extract the mean flow velocity and thus to evaluate an effective viscosity.
Phase behavior of confined melts of semi-flexible polymers: a Monte Carlo study

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We report on investigations of the isotropic-nematic phase transitions occurring in a confined melt of semi-flexible polymers by means of Monte Carlo simulations. We are employing the bond-fluctuation lattice model with stiffness induced by a fixed bond potential. Interactions between the chains and the flat walls are purely repulsive making this a model system for lyotropic isotropic-nematic transitions. The phase behavior of this system in the bulk had been studied by us before in detail [1, 2] as a function of chain stiffness and also with the inclusion of non-bonded attraction between the repeat units.

FIG. 1: Snapshot of a 60x60x500 box depicting the local orientation of bonds at a point (x,z). At the left and the right side are the two confining walls (z-direction). The bond orientation is averaged at fixed (x,z) over all y coordinates. If the resulting orientation is parallel to the confining walls the (x,z) pixel is colored either red (x-orientation) or green (y-orientation), if it is perpendicular to the walls it is shown in blue. Intermediate colors interpolate between those. Clearly, the layers at the walls are ordered, while the bulk is still isotropic.

The simulations are performed in the grand-canonical ensemble, i.e., the chemical potential \( \mu \) is a control parameter in the simulation changing the average volume fraction in the simulation box (geometry LxLxD, where D is the distance between the two repulsive surfaces). The repulsive walls have two influences on the adjacent polymer solution: i) there is an entropic attraction to the walls making the local density at the walls higher than the density in the center of the film and ii) chains adjacent to the walls are forced into an orientation parallel to the walls, i.e., the end-to-end vector of such chains is preferentially oriented parallel to the walls. At the walls we therefore have a 2d isotropic-nematic transition preempting the bulk transition, as shown in Fig. 1.

This leads to a surface-induced ordering phenomenon of the bulk, which can manifest itself in two ways [3, 4]: i) when we consider the limit \( D \rightarrow \infty \) and then \( \mu \rightarrow \mu_{\text{coex}} \) we observe a complete wetting
transition of the nematic layer at the wall and ii) when we consider the limit $\mu \to \mu_{\text{coex}}$ at fixed $D$ we observe capillary nematization, i.e., a shift of the location of the isotropic-nematic phase transition proportional to $D^{-1}$.

For a lattice model, the bond fluctuation model has a large degree of orientational flexibility, however, conformational entropy prefers the three lattice directions for the orientations of stretched out chains. The ordering transition of the bulk is therefore of 3-state Potts type and a 1st order phase transition, while the wall layer shows a transition of Ising type which is compatible with a second order transition. The 1st order transition in the Potts model is stable under application of an ordering bulk field (a possible description of the influence of the ordered surface) and so the transition survives as a function of $D$ but it changes its character when $D$ gets of the order of the extension of the stretched out molecules, because then only 2 of the 3 states can be populated. When the remaining two states are degenerate, there is a tricritical point and the transition continues as a 2nd order transition. With an effective ordering field induced by the nematic wall layers, however, the Ising symmetry is already broken, and the 1st order transition ends in a critical point with a line of rounded pseudo phase-transitions connecting the critical point to the surface phase transition.

Our model study thus provides a guidance how to interpret the effects of confinement onto the isotropic-nematic transition of semi-flexible polymer melts by exemplifying the statistical mechanics of ordering phenomena in such systems.

References:

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Segmental dynamics of interfacial polymer chains in nanocomposite hydrogels: From the nanosecond to the millisecond time scale

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Polymer hydrogels are defined as networks of hydrophilic polymers that contain a large amount of water while keeping a solid-like behavior at the macroscopic length scale. In order to improve their mechanical performances, inorganic filler nanoparticles were incorporated within these hydrogels. In contrast to bulk polymer matrices reinforced by nanosized inorganic fillers, the preparation of nanocomposite hydrogels is quite recent since the first contribution along this line was reported by Haraguchi et al. in 2002.1 In some cases, clay-based hydrogels with an excellent mechanical toughness together with an elastic behavior observed until a deformation ratio of about 10 were obtained. Interestingly, the tensile modulus was generally found to be an increasing function of the clay content. However, the molecular origins of the reinforcement of the mechanical performances obtained by adding clay layers within polymer hydrogels have not been yet extensively investigated. Recent studies2 on hydrogels based on poly(N,N-dimethylacrylamide) (PDMA) and silica have demonstrated that the enhancement of the mechanical performances resulted from strong interactions between the filler particles and the interfacial PDMA chains. Such a feature points out the significant role played by the polymer chains located at the surface of the filler particles. In the case of clay-based hydrogels, the progressive growth of clay platelet aggregates leads to a connected structure, the so-called "house of cards" structure. As a result, part of the polymer chains is expected to be constrained between both faces and edges of the clay layers. Similarly to the case of filled bulk polymer matrices, the local dynamics of such interfacial chains should be a key feature to get a better description of the increase of the Young modulus displayed by these hybrid hydrogels.

In the present work, hydrogels composed of poly(ethylene glycol) (PEG) chains and Laponite were considered. Combined solution and solid-state NMR approaches were used to probe the segmental dynamics of the PEG chains adsorbed on the clay platelets, over the nanosecond to millisecond time scale.

In a first step, the evolution of the PEG chain dynamics during the hydrogel formation was investigated. In particular, the level of local constraints undergone by the PEG chains was monitored through time-resolved 1H NMR experiments and a pronounced slowing-down of the segmental motions displayed by a fraction of the PEG chains was observed over a time scale $t_{\text{NMR}}$. This description at the molecular length scale was correlated to the variation of the rheological behavior related to the gelation phenomena, which is mostly governed by the assembling process of the Laponite disks. The shear storage modulus, $G'$, was found to increase over a time scale similar to $t_{\text{NMR}}$. Comparison between both kinds of measurements led to demonstrate that the observed slowing down of the segmental motions during gelation arises from adsorbed PEG repeat units or chain portions becoming strongly constrained between aggregated clay layers.
In a second step, the dynamical behavior (segmental dynamics) of these interfacial PEG chains was investigated through $^1$H, $^2$H and $^{13}$C solid-state NMR spectroscopy. Previous investigations based on neutron spin-echo experiments on similar systems evidenced that the constrained PEG repeat units were frozen over a few tens of nanoseconds. The PEG reorientational motions at the clay surfaces were probed over a longer time scale, given by several tens of microseconds, using $^1$H double-quantum (DQ) build-up curves. The $^1$H DQ signal detected in these PEG/Laponite hydrogels was found to arise from PEG protons of the interfacial chains or from pairs composed of one PEG proton close to the clay surface and a Laponite OH proton. Therefore, such measurements allow determining that PEG reorientational motions may be detected over several tens of microseconds. In order to describe the extent of this segmental mobility, a comparison with a model system of amorphized PEG chains in the bulk state was performed and led to the conclusion that the previously detected molecular mobility corresponds to rather restricted motions. At 300 K, the reorientational motions displayed by the adsorbed PEG chain portions in the hydrogels were found to be as restricted as the ones of bulk amorphous PEG chains, cooled at a slightly lower temperature (about 290 K). More quantitatively, complementary $T_2*^{(13}$C) and $T_1^{(13}$C) relaxation time measurements showed that the characteristic frequency of these segmental motions was found to range between 78.0 kHz and 100.7 MHz at 300 K.

In a last step, beyond the characteristic motional rate of the interfacial PEG chain motions, $^2$H NMR experiments performed on a hydrogel prepared with a perdeuterated PEG homopolymer were performed in order to get a more precise description of the geometry of these reorientations. The detailed analysis of these data in terms of motional models will be discussed.

References:
The dynamic and the glass transition of polystyrene in nanoparticles: the analogy with thin films

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The glass transition and the dynamic of confined polymers are key parameters for controlling the processing and stability of nanostructured materials such as nanocomposites, water-borne coatings and nano-electronics. In this work, we investigate the glass transition and the dynamic of confined polystyrene in nanoparticles. The polymer relaxation time is estimated from the closure of voids between close-packed particles (Figure 1).\textsuperscript{1-3} The time-temperature dependence of the relaxation time was investigated for various particle sizes in the glassy regime.\textsuperscript{4} The glass transition was investigated using calorimetry technique for freestanding and contacting particles. These results show that polystyrene in nanoparticles adopt all aspects of bulk behaviour in contrast with the findings on thin films.\textsuperscript{4,5}

![Small angle neutron scattering of polystyrene particles in the close packed structure, during their deformation under the surface tension stress.](image.png)
Figure 2. The time dependence of the relaxation time $\langle \tau \rangle$ of polystyrene in close-packed particles plotted against $1/T$ and compared to the bulk relaxation time. $\langle \tau \rangle$ is deduced from the dynamic of void closure (figure 1).

References

Crowded Colloids

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The entropic ordering of hard particles due to crowding has been known since the early works of Onsager on rods and Kirkwood on spheres. In this lecture we show how entropic considerations arising in crowded environments can produce complex crystals, liquid crystals, and even quasicrystals from hard particles due solely to particle shape. We introduce the concept of entropic patchiness and show how entropically patchy particles can be designed to assemble, upon crowding, into structures traditionally observed only with atoms.

Molecular motion in polymer thin films and at the surface of molecular glassformers

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This talk will discuss recent experiments that directly measure molecular motion in very thin polymer films near the glass transition temperature Tg. These measurements reveal the existence of a subset of polymer segments with mobilities that exceed bulk mobility by up to 4 orders of magnitude. Additional experiments will be presented in which molecular mobility is inferred by the response of the system to a surface perturbation. For low molecular weight glassformers near Tg, surface diffusion can be 7 orders of magnitude faster than bulk diffusion. These experiments will be interpreted in light of recent computer simulations that explore the impact of surfaces on the dynamics of glassformers, and also in light of the extensive literature on the Tg of thin polymer films.
We present a comparative study of the structural and dynamical properties of two series of 'comb-like' polymers: poly(alkylene oxides) and poly(n-alkyl methacrylates) (1-6). In both cases, polymers with increasing length of the side groups are investigated, being the difference between the two families the rigidity of the main chain. Different experimental techniques are employed, in particular including a variety of neutron scattering methods. These, together with isotopic labelling, have allowed us the selective investigation of main-chain and side-group properties. Self and collective motions are probed. In a complementary way, fully atomistic and coarse-grained molecular dynamics simulations have also been employed. The structural features developed in both series are identical, and are characterized by a nanosegregation of alkyl side groups and main chains. Contrarily, the dynamical properties of the side groups within the formed alkyl nanodomains are strikingly different depending on the main-chain nature. They show the typical signatures of confinement effects in high-order members of poly(n-alkyl methacrylates), which can be attributed to the development of a strong dynamic heterogeneity in these polymers. The purely entropic origin of the self-assembled nanostructures and the decisive influence of the dynamic asymmetry are confirmed by the coarse-grained simulations. References:

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Mechanical Properties of Thin Confined Polymer Films Close to the Glass Transition in the Linear Regime of Deformation: Theory and Simulations

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Over the past twenty years experiments performed on thin polymer films deposited on substrates have shown that the glass transition temperature $T_g$ can either decrease or increase depending on the strength of the interactions. Over the same period, experiments have also demonstrated that the dynamics in liquids close to the glass transition temperature is strongly heterogeneous, on the scale of a few nanometers. A model for the dynamics of non-polar polymers, based on percolation of slow subunits, has been proposed and developed over the past ten years. It proposes a unified mechanism regarding these two features.

By extending this model, we have developed a 3D model, solved by numerical simulations, in order to describe and calculate the mechanical properties of polymers close to the glass transition in the linear regime of deformation, with a spatial resolution corresponding to the subunit size. We calculate the evolution of the elastic modulus as a function of temperature, for different film thicknesses and polymer-substrate interactions. In particular, we show that for strong interactions and small thickness, glass transition is not only increased (by up to 20 K) but also broadened and accompanied by huge fluctuations of the storage modulus. This effect due to the low percolation threshold across thin films conjugated to the huge difference between high and low frequency moduli, should be more apparent in mechanical experiments than in dielectric spectroscopy or calorimetry.

![Figure 1: The shear modulus is simulated as a function of temperature for thin polymer films. The transition between the glassy and rubbery behavior occurs at a higher temperature in thin films provided polymer-substrate interactions are strong.](image-url)
Competitive effects in the dynamics of polymer nanocomposites

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Nanocomposites consisting of polymers reinforced with filler particles as carbon black or silica are important for a wide variety of industries and processes. Although these nanocomposites exhibit unique viscoelastic properties – and as such are widely applied in e.g. tires and sealings– the precise mechanism of the reinforcement is at best incompletely understood at present. Our research aims at understanding, and ultimately controlling, the macroscopic visco-elastic properties of such systems on the basis of both the microscopic intermolecular interactions and the mesoscopic structure of the composite. To this aim, we (a) simulate the structure and dynamics across many length scales, (b) probe the interactions between the filler particles and the polymer matrix, (c) relate these to the measured macroscopic mechanical properties. Our primary goal is to develop an improved understanding of the non-linear visco-elastic properties of reinforced rubber nanocomposites.

At high volume fractions the fillers connect to each other through polymeric bridges resulting in a percolation network. Its rigidity depends on the filler volume fraction and is breaking down under loading. We performed molecular-dynamics simulations of the dynamical behaviour of the inter-particle polymers using coarse-grained models of SBR or NBR polymer films of different thickness between attractive substrates. The polymer structure and segmental dynamics in different film layers has been analyzed. We found that increasing attraction strength leads to deceleration of the film dynamics due to a slowing down close to the substrates, but decrease of film thickness leads to an acceleration of this dynamics. We attribute this acceleration to finite-size scaling effects. For thick films an acceleration of dynamics in the middle takes place for sufficiently high attraction strengths due to the effective increase of the glassy layers thickness close to substrates. We will report the first results on simulation of mechanical properties (stress-strain curves, moduli) of cyclic shear behaviour of these films.
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The effect of constrained environment on the adsorption of proteins in nanopores with well-defined geometry has been explored. To this aim we have set up a procedure that allows building nanostructured membranes with well-defined architecture containing pores delimited by walls of controlled hydrophilicity/hydrophobicity exploiting self-assembly of block copolymers (BCP) and the concept of sacrificial block. Nanostructured thin films (thickness =65 nm) with lamellar morphology have been obtained by drop casting and/or spin coating dilute solutions of polystyrene-b-polylactide (PS-PLA) and mixtures of PS-PLA and polystyrene-b-polyethylene oxide (PS-PEO). In the case of the blend the morphology is characterized by PS lamellar domains alternating to layers of mixed PLA/PEO blocks (Figure 1A,B). We have demonstrated that the use of a PS-PLLA block copolymer containing a crystallizable poly-L-lactide (PLLA) block allows achieving a high degree of orientation of the lamellar morphology on the whole macroscopic surface exploiting directional solidification and epitaxy onto a hexamethylbenzene as substrate (Figure 1C,D).

Selective etching of PLLA blocks produces channel with width of 20 nm delimited by functional walls of PS lamellar domains with pendant PEO chains (Figure 2A,B) and tailored degree of hydrophilicity/hydrophobicity depending on the number density of PEO per unit area (Figure 2C,D). Absence of polylactide blocks and presence of PEO fringes after etching is also indicated by Raman spectra (Figure 2E,E’).
Matrix-Assisted Laser Desorption/Ionization (MALDI)-mass spectroscopy has shown that these nanoporous patterned surfaces constitute the ideal support for the physical absorption of proteins and enzymes (Figure 3).

Preliminary results of enzymatic reactions indicate that the BCP approach containing a sacrificial block for building nanoporous patterned surfaces is a robust and versatile tool useful not only in applicative research for fabrication of lab-on-chip nano-arrays of biosensors, but also in basic research to study the adsorption mechanism of proteins in constrained environment with controlled geometry at fundamental level.
In the tire industry, the incorporation of silica in rubber leads to elastomeric materials with enhanced mechanical properties: high rigidity and low hysteresis materials have an important contribution to the low rolling resistance of “green” tires. In a fundamental approach, two main contributions are commonly accepted to explain these changes: a first from the filler network highly depending on the silica aggregate dispersion, a second from the chains whose conformation is potentially modified by the filler network.

We work on model systems in which these two contributions can be studied separately by Small Angle Scattering. This technique has the interest to give structural 3D-information in reciprocal space, from local (≈1Å) to larger scales (≈1000Å).

On the one side, using either the neutronic or the electronic contrast existing between SBR and Silica, the filler dispersion can be measured as well by Small Angle Neutron Scattering (SANS) as by Small Angle X-Ray Scattering (SAXS). Besides, we use Transmission Electron Microscopy (TEM) as a complementary technique: it gives information on dispersion in real space which we can confront to the one obtained in reciprocal space by SANS or SAXS.

The filler in our model systems is a Ludox type nanoparticle, whose form factor $P_{NP}(q)$ is well defined by SANS or SAXS (Fig.1). Knowing this form factor, our analysis can be directly done in terms of structure factor $S(q)$, which characterizes the aggregation state.

The dispersion is tuned by two silanized agents, containing Ethoxysilane groups expected to graft on the silica surface (Fig.2). OCTEO is a covering agent: thanks to an 8-Carbon group, it enhances the filler/matrix compatibility by increasing favorable Van der Waals interactions. Si69 is a coupling agent, able to make covalent bonds between the filler and the chain thanks to Sulfur atoms.
On the other side, using the neutronic contrast between hydrogenated SBR chains and their deuterated homologs, we can measure the chain conformation in presence of silica by SANS in a specific condition: the Zero Average Contrast (ZAC) condition. In a three component mixture containing Silica, hydrogenated chains (H-SBR) and deuterated chains (D-SBR), the scattering can be written as follows:

$$I(q) = [(ρ_D - ρ_H)^2 * \varphi_D*(1-\varphi_D) * ν * (1-\varphi_{SiO2}) * N * P_{Ch}(q)]$$
$$+ [(\varphi_D * ρ_D + (1-\varphi_D) * ρ_H - ρ_{SiO2})] * [(ν^* (1-\varphi_{SiO2}) * N * P_{Ca}(q))] + ν^* (1-\varphi_{SiO2}) * S(q)$$

The first term is proportional to $P_{Ch}(q)$ which is the form factor of a single chain, the second one contains the silica-chain interaction factor $S(q)$. The Zero Average Contrast method consists in mixing H-SBR chains and D-SBR chains in such proportion $\Phi_D$ that the neutronic scattering length density of the mixture equals the one of silica $\rho_{SiO2}$, that means to reach the condition:

$$\Phi_D = 46\%$$

This condition is reached for $\Phi_D = 46\%$. Thus, the scattering of silica is matched and the silica-chain interaction factor $S(q)$ gets cancelled with the second term. The scattering is reduced to the first term, proportional to the form factor of a single chain $P_{Ch}(q)$.

In our systems, depending on the dispersing agents and the silica volume fraction, the primary fillers may form big aggregates separated by a distance d much larger than the radius of gyration of the chain $R_g$ (d/$R_g$>>1). This kind of dispersion has been studied by TEM (Fig.3a) and SAXS (Fig.3b), then we have investigated the effects of these dispersions on chain conformations in ZAC condition (Fig.4). This case of d/$R_g$>>1 corresponds to long range-effects on conformation.

As noticeable on TEM pictures (Fig.3a), primary nanoparticles are aggregated: this is a common observation for systems prepared by solvent casting. The $S(q)$ curves of silica (Fig.3b) allows us to describe more finely this aggregation. The shoulders at $q_s$, pointed by the blue and green arrows show that there are two levels of aggregation: nanoparticles form primary aggregates, which in turn form secondary aggregates. The $q_s$ values can be directly related to the distance between primary aggregates in contact. The higher $q_s$ value with Si69 shows that primary aggregates are smaller with Si69 than with OCTEO. For $q_s$ values, we can describe the structure of the secondary aggregates: the slope of $S(q)$ is directly linked to their fractal dimension, the value of $S(q)$ toward small $q$ to their size. The higher slope and the higher value of $S(q)$ toward small $q$ for Si69 show that secondary aggregates are denser and bigger than with OCTEO.

To sum up, for the first level of aggregation, Si69 leads to smaller objects than OCTEO; the contrary is observed for the second level of aggregation.
Fig. 4a shows the SANS measurements in ZAC condition associated to these dispersions; Fig. 4b shows their respective fits (plain curves, vertically shifted for an easier reading). On Fig. 4a, for \( q > q^* = 0.015 \text{Å}^{-1} \), spectra are perfectly overlaid and correspond to the form factor of a single chain. That means that for size smaller than \( R_g \) (70Å), silica is correctly matched and we measure the chain form factor \( P_{Ch}(q) \): it is unchanged compared to in pure matrix (open black squares), whatever the silica dispersion. However, for \( q < q^* \), we observe an additive scattering. On Fig. 4b, we model it by the scattering of large domains (≈400Å) of demixed H-SBR and D-SBR chains. A very small amount of these domains (ranging from 0.01 to 0.1%) is enough to induce this additive scattering; size and amount of these domains are depending on the dispersion.

In summary, apart of these domains, the chain form factor is unchanged while the silica dispersion can be varied substantially through the use of the agents.

The filler network has no long-range effect on the chain conformation; the chain is not pre-strained by the filler network at rest which is an important information for mechanical behavior.
Heterogeneous dynamics in a thermosensitive soft suspension

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Dense colloidal suspensions are ideal model systems to study the glass transition. With increasing volume fraction, the suspension dynamics experiences a slowing down of several orders of magnitude, as well as a change of qualitative behavior, from viscous to elastic, at reasonable experimental time scales, and with no significant structural changes. Hard-sphere suspensions have been extensively investigated for their relative simplicity in modeling the glass transition. Recently, soft colloidal suspensions have also attracted attention. They can be designed with various particles softness (and interactions), allowing for a wide variety of behavior in mimicking the glass transition in traditional glasses.

We have investigated the dynamic heterogeneities of soft thermosensitive microgels suspensions. The microgels can be designed with various softness, depending on the cross-linker density. More importantly, the particles radius in the suspension, and therefore their volume fraction, can be reversibly tuned with temperature, which provides a unique way to explore the phase behavior on the same sample.

The suspensions heterogeneous dynamics was first characterized by looking at the thermal fluctuations of probe particles, since the microgels were almost index matched, and thus impossible to visualize under the microscope. When approaching the glass transition, the dense colloidal suspensions were found to develop a spatially heterogeneous dynamics, featured by fast and slow domains coexisting through the sample, on relatively short time scales. We have characterized the distribution of these domains of different dynamics through the sample, at equilibrium and out-of-equilibrium.

In suspensions with particles exhibiting a higher cross-linking density, and thus visible under the microscope, we have measured spatial correlations through the sample using image correlation techniques. A growing correlation length of these domains was extracted with increasing volume fraction.
Colloidal Osmotic Bulk Modulus of Polymer-Crowded Colloidal Suspensions

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Introduction:
By adding non-adsorbing polymers to a colloidal suspension, the mixture can phase separate into polymer-rich and colloid-rich phases. This phenomenon can be explained by a polymer crowding induced attractive force between colloidal particles. While the concept that polymer crowding can induce attraction between particles is simple, it is far from simple to quantify the crowding-induced force because the crowding-induced attraction depends on the chemistry of the particle surface, solvent quality, and for charged particles or polymers, the Coulomb interactions. This paper reports a study that determines the interaction potential in terms of colloidal osmotic bulk modulus. Colloidal osmotic bulk modulus of polystyrene nanoparticles in a high salt and polymer-crowded solution has been determined as a function of PEG concentration. The study was enabled by a new method called optical bottle that analyzes the statistics of the transient, multiply trapped colloidal nanoparticles in optical confinement to determine the osmotic bulk modulus.

Methods:
Optical bottle is a technique that uses a highly focused IR laser beam to transiently trap an ensemble of nanoparticles against the osmotic pressure gradient created by the enriched particle concentration in the trap area. Under constant laser power, a steady-state concentration gradient is established by the balance between the osmotic pressure of the pressure created by optical gradient force. We determine the latter by experiments at low particle concentrations and high salt so that particle interactions are negligible and the system can be regarded as an ideal gas. Once the optical force on the nanoparticles is known, it can be used to determine the osmotic compressibility of the colloidal particles from the spatial distribution of the particle concentration obtained by fluorescence confocal microscopy. In this study, we use suspensions of 200 nm fluorescently labeled polystyrene particles as a model system for investigating how interactions between the particles are altered in the presence of polyethylene glycol (PEG). The enhancement of the concentration of the fluorescence particles in the trap can be controlled by the trapping laser intensity. Since the 3D fluorescence confocal image shows that the enhancement of particle concentration is confined in the region defined by the (0.5x0.5 x 3 micron) area of the focal point of the laser.

Fig. 1. The experimental setup for an optical bottle. The lower microscope is a confocal laser scanning fluorescence microscope.
Results:
Fig. 2.1 shows a 3D fluorescence image of 200 nm PS particles in and around the focal point of the 1064 nm trapping laser. Constant-z cut across the maximum fluorescence intensity of the 3D fluorescence image yields the 2D concentration profiles $N(x, y)$. Fig. 2.2 is a plot of the normalized concentration $N(r)/N_0$ vs. $r$ where $r$ is the distance from the center of the trap. $N(r)$ is obtained by taking an average over all $N$'s at a same distance $r$, and $N_0$ is the mean value of $N$ from points far from the center of the trap. The data taken at sufficiently low particle concentrations, such as the top two curves in Fig. 2.2, can be assumed to follow a Boltzmann distribution, i.e., the particles are ideal like because the contribution of the particle interactions to osmotic compressibility is negligible. The bottom five curves are data taken for $N_0$ that is ten-times higher than the top curve; they are lower because the osmotic compressibility decreases with increasing concentration. Fig. 2.3 is the trapping energy distribution profile (in unit of $k_BT$) determined by $U(r) = \ln(N(r)/N_0)$ from the top curve in Fig. 2.2. Fig. 2.4 is the single-particle trapping force profile determined by $F(r) = dU(r)/dr$.

Since the deviations from the Boltzmann distribution of particles in the trap at high concentrations are caused by particle interactions, we can quantify the particle interactions in terms of colloidal osmotic isothermal compressibility $\beta^{(1)} = \langle U(r) \rangle / k_BT$. Identifying $dP/d\tau = N(\tau)F(\tau)$, we calculate the compressibility from the measured values: $\beta^{(1)} = \langle \delta N/\delta r \rangle / \langle F(\tau)N^2(\tau) \rangle$. From $\beta^{(1)}$ and $N(\tau)$ we determine the colloidal osmotic bulk modulus $\beta(N) = 1/\langle \delta N \rangle$: shown in Fig. 2.5. Virial expansion of the osmotic bulk modulus yields $1/\langle \delta N \rangle = 1 + 2B_2 + 3B_3 + O(N^2)$. Fig. 2.6 shows $2B_2 + 3B_3$ vs. $N$, where we see $B_2$ (intercepts/2) decreases with increasing PEG.

Conclusions:
Using the optical bottle method, we measured the osmotic bulk modulus of the polystyrene nanoparticles as a function of PEG concentration. Our results show the osmotic bulk modulus decreases with increasing PEG crowding. Second virial coefficient, obtained from the virial expansion of the osmotic bulk modulus, also decreases with increasing PEG concentration, revealing the expected, polymer-induced attraction between the PS nanoparticles.

Acknowledgments:
The research is supported in part by a grant from the National Science Foundation DMR-0923299 and the Emulsion Polymers Institute, Lehigh University.
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Effect of confinement and wall roughness on colloidal suspensions at low Peclet numbers

Somnath Ghosh
Physics of Complex fluids – University of Twente

We studied the flow of hard sphere colloidal suspensions in microchannels having both smooth and rough walls. We use CSLM to image 1 μm silica spheres (FITC fluorescence in the core) suspended in Methanol-Bromoform solvent mixture as well as Glycerol-water solvent mixture. We mainly focus on the flow patterns and concentration profiles of the suspensions in the low Peclet number (Pe) regime. Our observations contrast to the findings in literature at larger Peclet numbers, where the particles migrate from high shear zones to low shear zones, resulting in higher particle concentrations at the channel center\textsuperscript{2,3}. Theoretically, it has been predicted that at low Pe, the particle concentration inside the microchannel should be homogeneous\textsuperscript{4}. We found inhomogeneity in concentration profile at the low flow regime. Furthermore we found a reduction in particle concentration at the channel center (as compared to the wall). We also observed that the apparent diffusivity of the particles at the center of the channel increases with the flow rate (Pe ~ 0 to 20). And finally we observed that the roughness on the wall reduces the slip.

References:
The mechanical properties of commercial polymer-matrix nanocomposites can be improved by adding fillers to polymer systems. There is still lack of quantitative relationships between the structure and mechanical properties of polymer-matrix nanocomposites to the chemical constitution and interactions of the macromolecules and nanoparticles of which they are composed. Our primary goal is to develop an understanding of the nonlinear elasticity of elastomer-based nanocomposite materials, aiming at disentangling the different contributions to the visco-elastic properties. In this paper we study tunable model system made of hard silica particles of controlled surface chemistry in a polymer matrix, by performing molecular-dynamics simulations of their (linear and nonlinear) visco-elastic properties. The relevant parameters are notably the filler/matrix composition, the polymer network structure and the particle/polymer interaction. The main focus will be on systems where the radius of gyration of polymer network subchains, $R_g$, and the distances between nanoparticle surfaces, $d$, are comparable. The projected insights into these systems are essential to the development of e.g. environmentally more friendly (‘green’) tires, elastomeric sealants and other advanced rubber materials.

We set up atomistic molecular-dynamics simulations using the Gromacs simulation engine of polymer films separating the surfaces of neighboring nanoparticles. A sample of non-crosslinked polymer (cis-1,4 polyisoprene) film confined between, but not chemically connected to, flat solid surfaces (amorphous silica) of composition mimicking that of the surfaces of the nanoparticles of interest has been prepared. In addition, bulk specimens of cis-1,4-polyisoprene have been simulated using the same united-atom force field. The thermodynamic (volume as a function of temperature), conformational (torsion angle distributions), and dynamical properties (orientational correlation functions for various bonds and associated correlation times at various temperatures) of the bulk polymer are in very good agreement with previous simulations and with experiment. Layer structure and dynamics in polymer films will be discussed. We will quantify their anisotropic structure, dynamics, stress state, and stiffness starting from the chemical constitution of the polymer matrix and the nanoparticle surfaces. Our focus here is on understanding the so-called Payne effect: the reversible loss of rigidity at larger strains and the associated viscous energy losses. Also the Mullins effect will be analyzed: the irreversible and strain-history dependent softening of the filled elastomer. Both effects are practically very important and are believed to be associated with weakening filler-filler and polymer-filler bonds, but conclusive experimental evidence at the required length scales is lacking.

Broadband Dielectric Spectroscopy (BDS) – in combination with a nanostructured electrode arrangement – is used to study thin layers of poly(cis-1,4-isoprene) (PIP). Being a Type A polymer, PIP enables the investigation of two distinct relaxation modes taking place at two different length scales: the segmental motion which involves structures of about one nanometer in size and the normal mode which represents the global dynamics of the chain. For molecular weights (24.5, 44.5, 53 and 75 kg/mol) much greater than $M_c$ (the critical molecular weight, $M_c = 10^4$), down to thicknesses comparable to the respective radii of gyration, it is observed that: (i) the segmental mode as a local relaxation process is unaffected by the confinement in thin layers; (ii) the normal mode becomes faster with decreasing layer thickness, and (iii) this change in the normal mode is molecular-weight dependent. For $M^\sim M_c$, both the segmental and normal modes remain unaffected by changes in layer thickness.
In this talk we will discuss the creation of a new novel material consisting of thermal sensitive suspensions for thermal-thickening purposes. Thermal-thickening suspensions have a wide range of applications such as oil recovery, paint, and home and personal care products. These suspensions are made of core-shell colloidal particles, the core is made of poly(methyl methacrylate) (PMMA) while the shell is made of thermosensitive poly(N-isopropylacrylamide) (pNIPAam). The core shell colloidal particles have thermal-dependent and salt-dependent interparticle interactions without a significant change to the volume fraction. When salt of certain concentrations were added to screen the electrostatic repulsion partially or completely, a reversible temperature-induced sol-gel transition was observed under optical microscope around lower critical solution temperature (LCST) of pNIPAam (32 °C). The suspension’s rheology behavior was further studied at different volume fractions and salt concentrations. A few orders of magnitude increase of both storage modulus (G’) and loss modulus (G’’) were observed as the temperature increased above the LCST, indicating a liquid to soft glass phase transition. Furthermore, the evolution of the interparticle interaction was evidence by the appearance of a yield strain and yield stress.
Phase separation dynamics in polymer blends close to Tg: aging and rejuvenating

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We extend the Percolation of Free Volume Distribution (PFVD) model developed by Long and co-workers [1, 2] to deal with polymer blends dynamics close to the glass transition. The dynamical model incorporates an extension of the Flory Huggins model to the case of compressible blends for calculating the driving forces. Spatial dynamics follows then from an Onsager like description [3]. The model is based on the strongly heterogeneous nature of the dynamics close to Tg on a scale of few nanometers (ξ of order 3-5 nm) [4, 5]. Dynamical heterogeneities are enhanced in polymer blends as compared to pure polymeric liquids as a consequence of concentration fluctuations. These dynamical heterogeneities are essential for describing components inter-diffusion. The model is solved on a 2D lattice corresponding to spatial scales of about a few tens to 100 nm and a resolution corresponding to the scale of dynamical heterogeneities. We apply this model to study phase separation close to Tg. During phase separation e.g. after cooling the system, we observe the formation of complex morphologies where slow domains are in coexistence with faster ones. The domains size grows like the logarithm of time as a consequence of the slow domains aging process, in agreement with experimental results obtained by Royston et al [6]. Then, we compare the phase separation dynamics to the reverse process, after the temperature is increased again in the totally miscible range. This process is analogous to the rejuvenating process as described by Kovacs in pure polymers. In this situation, we observe also a temporal asymmetry between the aging and the rejuvenation dynamics: the slow domains melt much faster than the elapsed time required to build them during the separation process and total miscibility is recovered after a much shorter time. We have characterized this temporal asymmetry by studying the effect of waiting time during the aging process, temperature and composition on the rejuvenation dynamics. The qualitative prediction of the model could be checked by neutron scattering or dielectric experiments, which would also help to calibrate the adjustable parameters of the model and to validate its underlying physical assumptions.

References :
Inter and intra-molecular dynamics of polymethylphenylsiloxane under 1-D and 2-D confinement

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Broadband dielectric (BDS) and Fourier transform Infrared (FTIR) spectroscopy are employed to study molecular dynamics of polymethylphenylsiloxane (PMPS) in 1-D and 2-D geometrical constraints. PMPS under the former confinement of thin films down to thickness of 7 nm spin cast on highly conductive silicon wafers in combination with nanostructured counter electrodes are studied by BDS while in the latter case, PMPS infiltrated into porous silica membranes with unidirectional nanopores having diameters down to 4 nm are probed by both BDS and FTIR. The glass transition temperature (Tg) of thin films for all the thickness investigated remained bulk-like but the Tg decreased with decreasing pore sizes for 2-D confinement where additional interfacial relaxation process is observed. This change in Tg is attributed to reduction of density of bulk-like molecules at the center of the pores. The intra-molecular IR vibrations of different moieties show dissimilar T-dependencies with little influence of confinement. The intermolecular dynamics is therefore impacted by the dimensionally of confinement.
Effect of Shear Processing on Structure and Mechanical Properties of Styrene Butadiene Triblock Copolymers

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Polystyrene/Polybutadiene based triblock copolymers having different middle and outer block composition and their blends with a phase separated lamellar morphology are processed at different steady shear flow conditions using a capillary rheometer. The shear flow in the melt induces orientation of the microdomains and morphology with macroscopic anisotropic properties. The primary objective of this research is to study the correlations between shear induced molecular arrangements, microstructure formation and their influence on the macroscopic mechanical properties of the block copolymers. Small angle x-ray scattering (SAXS) and transmission electron microscopy (TEM) techniques are used to study the orientation behaviour of the microstructures. It has been found that the structures are strongly oriented along the shear flow direction. From TEM analysis it is observed that the main effect of shear flow to align the ordered lamellae in parallel orientation with long-range order is mainly at low shear rates. However, the long-range ordered lamellae are transformed to short-range ordered one at high shear rates. The macroscopic mechanical properties of the shear aligned block copolymers are investigated through probing the stress-strain behavior and compared with non-aligned one. A linear dependency of Young’s modulus and yield stress is observed for samples processed at different shear rates. Young’s modulus changes from 1080 ± 50 to 500 ± 20 MPa for samples processed at 5 s⁻¹ and 600 s⁻¹ shear rates respectively.
Entanglement-induced reinforcement in polymer nanocomposites

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We propose a coarse-grained model able to describe filled entangled polymer melts. Our purpose is to study the reinforcement caused by the effect of fillers on the entanglement network as speculated in Ref. [1] and glimpsed from Molecular Dynamics [2–5]. In this work, the filler volume fraction effect, the distribution of the fillers (cubic lattice, random, and small cluster) and the presence or not of grafted chains on the fillers are investigated. This model is based on the "slip-link" models initially developed to study the entanglements in pure polymer melts and offering a less costly computational method than the Molecular Dynamics simulations ([6–13] and [14]). In our model, based on the "slip-link" model developed by Likhtman [13], the polymer chains are described as Rouse chains of Brownian particles connected by Hookean springs, and submitted to friction and random forces. Entanglements are artificially imposed by statistical fluctuating objects (i.e. slip-links) which ensure that the equilibrium statistics are not affected. In addition we introduced excluded volume interactions between chain segments, as done in Ref. [14], in order to take into account density inhomogeneities produced by the nanofillers. These excluded volume interactions do not perturb the dynamics of the chains in the homogeneous limit [14] as expected from theoretical considerations on short range interactions [15]. Finally, the fillers are modeled by immobile spherical objects, with or without grafted chains, which interact with a repulsive potential with the chain monomers. The grafted chains are represented by "additional slip links" confined in a certain region around each filler. We first present the effect of the filler distribution and filler volume fraction, considering only bare fillers. Then, the effect of grafted chains via the additional slip-links is also shown as a function of the same parameters. We vary the number of additional slip-links between 50 and 200 per filler where 100 corresponds to the typical number of slip-links (i.e. entanglements) at the given density of monomers in our system without fillers.
References:
Local and global dynamics in thin layers of poly(cis-1,4-isoprene)

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Broadband Dielectric Spectroscopy (BDS) – in combination with a nanostructured electrode arrangement – is used to study thin layers of poly(cis-1,4-isoprene) (PIP). Being a Type A polymer, PIP enables the investigation of two distinct relaxation modes taking place at two different length scales: the segmental motion which involves structures of about one nanometer in size and the normal mode which represents the global dynamics of the chain. For molecular weights (24.5, 44.5, 53 and 75 kg/mol) much greater than $M_c$ (the critical molecular weight, $M_c = 104$), down to thicknesses comparable to the respective radii of gyration, it is observed that: (i) the segmental mode as a local relaxation process is unaffected by the confinement in thin layers; (ii) the normal mode becomes faster with decreasing layer thickness, and (iii) this change in the normal mode is molecular-weight dependent. For $M \sim M_c$, both the segmental and normal modes remain unaffected by changes in layer thickness.
Multiscale modeling of the polymer-filler interaction

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Filled elastomers systems are extensively used in the rubber industry for the reinforcement of the polymer matrix. Nowadays, both organic and inorganic fillers are used to improve the properties of rubber materials. In spite of visible change in properties at a macroscopic level, as for example an increase in the shear modulus, an accurate description of mechanisms that are associated to this reinforcement is still missing. Nevertheless, it is known that the spatial distribution of the fillers is of high importance for the reinforcement of the rubber materials [1]. Analytical calculations show that this spatial distribution is governed by the effective polymer- mediated filler-filler interaction [2]. The latter effective potential is highly dependent of the polymer-filler interaction, which is difficult to describe quantitatively.

A way of considering the polymer-filler interaction is to use current simulation tools to study the motions of such a system. However, polymeric systems have various kinds of motions and a multiscale approach is required to sample the largest length and time scales. Microscopic simulations using atomistic models are used to perform the calculation of potentials of mean force. These potentials can be used to describe polymer-filler interaction at a mesoscopic scale using the Dissipative Particle Dynamics (DPD). DPD has been used at the beginning with generic potentials that were not designed for modelling polymer of a specific chemistry. The way of developing the potentials (i.e. at constant pressure using the iterative Boltzmann inversion) allows conserving the chemical nature and the thermodynamic conditions of the system. Initially, the study was performed on a polybutadiene bulk matrix in order to validate this method [3]. It is then extended for quantitative predictions to a composite model that consists of two planar fillers of silica confining several chains of polymer, grafted or not.

References:
Structure-property relationships of polymer nanocomposites based on recycled polyethylene terephthalate and montmorillonite clay

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INTRODUCTION
Polymer nanocomposites belong to one of the most rapidly growing classes of novel materials. Due to their outstanding properties polymer nanocomposites increasingly often substitute traditional materials in many branches of national economy, such as automotive, building, sport, food and other sectors. Investigations in the field of polymer nanocomposites as well as their application in different fields of national economy presently are connected with the systems based on primary polymers. By considering increased use of polymer nanocomposites one should account for generation of substantial polymer nanocomposite waste stream in the closest future. Consequently investigations of polymer nanocomposites based on post-consumer polymers as well as evaluation of recyclability issues of polymer nanocomposites gain increasing attention.

EXPERIMENTAL
In the current research structure and properties of the nanocomposites based on recycled poly(ethylene terephthalate) (RPET) are discussed. Unmodified montmorillonite clay (MMT) as well as organically modified montmorillonite clay (OMMT) are used as nanofillers in the weight amounts of 1-5 %. Advantages of using unmodified nanofiller are smaller expenses as well as better thermal stability, significant in the case of multiple processing, unavoidable at recycling. Main advantage of using organomodified nanofiller is better compatibility between polymer matrix and OMMT, leading to increased overall properties of the nanocomposite. Nanoclay modified RPET nanocomposites are compared with those based on primary polymer (PET). Nanocomposites have been obtained by using melt compounding in a twin-screw extruder. Structure and exploitation properties of the nanocomposites have been investigated by using following methods: electron microscopy, differential scanning calorimetry, quasistatic tensile testing, dynamic mechanical thermal analysis, instrumented impact strength analysis, thermomechanical analysis and thermogravimetric analysis.

RESULTS
Results of the investigations testify that the optimum content of nanoclay for modification of either RPET or PET is between 1-2 wt. %. Up to this nanofiller weight content, the most rapid increase of elastic modulus, stress and impact strength is observed. As it is shown in Fig.1 the effect of nanoclay on the properties of the investigated nanocomposites in general is rather equal regardless of polymer matrix used. It is also worth mentioning that modification effect of OMMT is somewhat greater in comparison to MMT, especially at higher nanofiller weight contents. Evidently this testifies about better distribution of the nanoclay in the thermoplastic polyester matrix. It is also important to mention, that nanoclays, acting as nucleants, considerably affect crystallization behaviour of the nanocomposites, especially in the case of RPET based systems as shown in Fig.2. Some of the representative results of the investigation are shown below.
Fig. 1. Stress-strain characteristics of the investigated nanocomposites: a- modulus of elasticity; b- strength at yield; c- strain at yield.

Fig. 2. Degree of crystallinity of PET (a) and RPET (b) ($\chi$) as functions of MMT content in the inner and outer regions of the impact test bars.
Ring Polymers in Gel: Topology and Dynamics

Davide Michieletto, Prof. Matthew Turner, Dr. Gareth Alexander,
Dr. Davide Marenduzzo

Since the pioneering work of Edwards and de Gennes the dynamics of polymers in melt has been understood using the tube and the reptation models. However, ring polymers continue to present a challenge to the theoretical community as they behave differently from their linear counterpart[1]. In order to study inter-ring interactions, we simulate a concentrated solution of unknotted, unlinked rings diffusing within an ideal gel, made up of a three-dimensional cubic lattice of (static) polymer segments with lattice spacing equal to the chain’s Kuhn length, see Fig. 1a. Each ring visits many unit cells, and therefore more closely resembles a branched polymer than a crumpled globule[2]. The topology of closed loops allows inter-ring threadings, or penetrations. We exploit the ordered architecture of our gel to unambiguously identify inter-penetrating rings, see Fig. 1b, which we show to have a life-time that is at least comparable to that of the longest relaxation time of the chains and may be much longer for longer chains. We suggest that, in the limit of very long chains, a percolating cluster of threading rings may arise, which would then exhibit very slow (glassy) dynamics at the scale of centre of mass motion for each chain, while retaining substantially unhindered motion at the level of individual chain segments. Our primary result is that we found that the probability of a ring of being threaded seems to increase linearly with its length, a trend which strongly supports the existence of the above mentioned topological glass transition, although the transition itself would occur for chain contour lengths that are much larger than those reached in our simulations.

Figure 1: (a) Snapshot of our system. (b) Snapshot of a two chains configuration where the blue one is threading through the red one inside of one cubic lattice cell, bounded on the edges by gel polymer. Light red and light blue dotted lines indicate the asymptotic closure construction that we employ in order to identify threading, using a standard topological measure of contour linking.

References:
Influence of Silica Nanofillers on Polymer Dynamics and Reinforcement of SBR Nanocomposites

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Mechanical properties of styrene butadiene rubber (SBR) nanocomposites filled with different amounts of silica nanoparticles are investigated by dynamic shear measurements and solid state NMR. Aim is to understand the micro-mechanical mechanisms affecting the viscoelastic properties of silica-filled elastomers and the results are discussed in the framework of filler network effects and an immobilized layer close to filler surfaces. In fig-1, shear data show that an increase in the volume fraction of nanoparticles not only affects the reinforcement and plateau modulus but also energy dissipation in the plateau range. It is also indicated in fig-1 that the glass temperature and frequency-temperature position of the main transition $\alpha$ of the SBR matrix, however, are not much affected [1]. Low-field NMR studies indicate the existence of a presumably surface-associated, immobilized and glassy polymer fraction which decreases with temperature. This temperature dependent glassy fraction affects not only the strength of filler network but also its time-dependent response in the plateau range.

Different contributions to reinforcement are quantified based on dynamic strain sweeps (fig-2) performed at different temperatures. Linear response results ($\gamma \rightarrow 0$) exhibit a solid 'filler network' incorporating filler particles. This filler network contributes strongly to reinforcement above the temperature-independent percolation threshold at $\phi_{\text{percol}} \sim 0.15$. A vertical dash line in fig-3 represents percolation threshold of filler network at 25°C and 60°C. Nonlinear dynamic measurement at large oscillatory deformations ($\gamma \rightarrow \infty$) breaks down the filler network and the remaining reinforcement (blue triangles in fig.2c and 2d), higher than the theoretical predictions, is interpreted as a result of occluded rubber within the broken filler clusters shielded from the applied stress field [1]. At high temperatures ($\sim 150^\circ$C), this remaining reinforcement i.e. $G'_{\gamma \rightarrow \infty}$, decreases and modulus values confirm the Guth-Gold prediction.
Fig 1: Master curves of (a) storage and (b) loss modulus for composites containing different amounts (0-80 phr) of silica U7000GR. The original isotherms are only horizontally shifted. Three different dissipation regimes in the loss modulus at different frequencies are indicated by labels corresponding to α peak, α’ wing, and low-frequency dissipation (LFD) regime. Reference temperature is 0 °C. [1]

Fig 2: Storage modulus $G'$ versus shear strain amplitude $\gamma$ (Payne effect) for composites containing different amount of silica at (a) 25°C and (b) 60°C. The lines are fits based on the Kraus model. Analysis of the corresponding strain sweeps is shown as a comparison of storage moduli at $\gamma \rightarrow 0$ (red circles) and $\gamma \rightarrow \infty$ (blue triangles) for different silica filled nanocomposites at (a) 25°C, and (b) 60°C. The thick dash line (green) and the dash dotted line (magenta) represent the prediction of GG and ES model respectively. The diagonal hatch shows the limit of unfilled SBR plateau modulus. The vertical dash line (violet) around $\Phi = 0.15\%$ at each temperature illustrates the percolation threshold limit of filler network. [1]

Nonlinear rheology of model filled elastomers – interpretation with a glassy bridges model

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The addition of solid particles in an elastomer matrix modifies the behaviour of the polymer chains in a complex way and thus transforms the mechanical properties in a non-trivial manner. Submitted to large sinusoidal strains, filled elastomers not only show a decrease in their storage modulus — the Payne effect - but also a nonlinear behaviour: their response is not sinusoidal anymore. In this study, we interpret the nonlinear mechanical behaviour of model filled samples with the reinforcement model proposed by D. R. Long et al. and based on the presence of glassy bridges linking neighboring particles [1].

Glassy bridges reinforcement model
The model is based on the presence of a glassy layer around the fillers - when the interaction between the filler and the polymer is strong enough - which can link neighbouring particles through a glassy bridge and thus explain the reinforcement. When the sample is solicited, the stress is concentrated on the solid skeleton formed by the bridges. The local stress increase can lead to a yielding of the bridges and thus a lowering of the shear modulus, which is observed in the Payne effect. In the model proposed here, the glassy bridges are represented by springs with a finite lifetime. The simulations account for the reinforcement, the Payne and Mullins effects. We will see here that it can also account for non-sinusoidal signals measured on model filled samples in high amplitude oscillatory shear.

Model filled elastomers
The model filled elastomers consist of grafted spherical silica particles dispersed in a poly(ethylacrylate) matrix [2]. Two kinds of grafter have been used: TPM (3-(trimethoxysilyl) propyl methacrylate), which can react with the monomer and thus create a covalent bond with the matrix, and C8TES (n-octyltriethoxysilane) with which there are only hydrogen bonds between the residual –OH groups on the silica surface and the polymer. The silica particles are 30 nm, 50 nm or 100 nm in diameter and the silica volume fractions of the samples are comprised between 10% and 30%.

Nonlinear mechanics: link with the presence of glassy bridges
We studied the nonlinear mechanical properties of our model systems using rheometry. We were able to measure the Payne effect - a decrease in the elastic modulus when the strain amplitude exceeds a few per cents. At higher strain amplitude, we observed that, even if the strain signal is sinusoidal, it is not the case of the stress signal [3]. The stress signal can be decomposed into elastic and viscous parts. The elastic part shows a strain hardening at the extremities of the strain cycle. This can be explained by a lower shear rate at this position and thus longer the relaxation time for the glassy bridges to rebuild. The viscous stress

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shows a maximum of dissipation for intermediate shear rates. The dissipation increases first linearly with the shear rate, then at larger shear rate, the kinetics of rupture and rebirth of glassy bridges is modified and the system becomes less dissipative [4].

We see here that the glassy bridges reinforcement model can account for the non-sinusoidal stress signal measured in large amplitude oscillatory shear experiments through the kinetics of rupture and rebirth of these glassy bridges.

References:
Constrained polymers in multiphase materials: NMR investigations of interphase structure and dynamics

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The mechanical properties of nanostructured functional polymeric materials crucially rely on the arrangement, structure and in particular connectivity of hard (undeformable) phase components, such as crystallites or filler particles in semicrystalline polymers or particle-filled elastomers, respectively. In addressing connectivity, constrained polymer chains and dynamic interphases often represent a prominent fraction of the overall matrix material. NMR is a well-suited technique to study the structure and the dynamics of such constrained phases with molecular resolution, possibly using simple low-field equipment.

In this presentation, I will present recent results on immobilized interphases arising from adsorption or binding of chains to filler particles or polymer crystallites. Recent strong evidence has been gathered on the existence of a glass transition temperature gradient in such systems, being responsible for the complex thermomechanical behavior of filled rubbers in particular. Our new work reveals that such interphases (also the "rigid amorphous phase" in semicrystalline polymers) do not form a contiguous layer around rigid filler particles or crystallites, but reside in island-like regions such as concave structures of a rough filler/crystallite surface. The phenomenon may be related to the requirement of stronger higher-dimensional constraints rather than a flat interface, or to the general nanoscale dynamic heterogeneity of polymers close to Tg. The phenomenon appears of general nature, and was also confirmed for interphases in diblock copolymers such as PS-PB.
Glass transition in ultra-thin films measured by differential AC-Chip Calorimeter

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The film thickness dependency of glass transition thin films is still controversially discussed, e.g. [1, 2]. For different experimental probes different dependencies are observed and a generally accepted link to molecular mobility is not yet established. Calorimetry has proven to provide useful information about glass transition, because it establishes a direct link to energetic characterization. In several cases a direct comparison with results from other dynamic methods like dielectric spectroscopy is possible giving further insights. For thin films in the μm...nm range standard calorimetric methods are mostly not applicable. In the recent years there are new developments in the field of calorimetry which overcome these limitations [3].

We set up a differential AC-chip calorimeter capable to measure the glass transition in nanometer thin films with pJ/K sensitivity in a relative broad frequency range [5-7]. Frequencies from about 1 Hz up to 10 kHz are accessible. Changes in heat capacity can be measured for sample masses below one nanogram [4]. For different materials thin films down below 10 nm are measured. The dynamic glass transition shows no influence from the film thickness in all measured samples. This is shown for different frequencies in the activation diagram (Figure 1) and at constant frequency as film thickness dependence (Figure 2).

\begin{figure}[h]
\centering
\includegraphics[width=0.4\textwidth]{activation.png}
\caption{Activation diagram for the glass transition of the films of different thickness. The solid lines are VFT curves, the dashed lines indicate the error limits of +/- 3 K.}
\end{figure}

\begin{figure}[h]
\centering
\includegraphics[width=0.4\textwidth]{film_thickness.png}
\caption{Film thickness dependence of glass transition temperature for different polymers at constant frequency.}
\end{figure}
The glass transition in thin films was determined at well-defined experimental time scales. No thickness dependency of the glass transition temperature was observed within the error limits - neither at constant frequency nor for the traces in the activation diagrams.

References:
Mesoscale modelling of reinforcement and non-linear properties of filled elastomers

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Elastomers filled with nanometric solid particles or aggregates show an ensemble of properties which are qualitatively different from the behaviour of the pure elastomer matrix: reinforcement of the modulus in the linear regime, with very strong temperature dependence; large non-linear effects and complex dissipation phenomena as the strain amplitude increases (Payne effect). All these phenomena can be rationalized by the effect of the glass transition temperature shift of the elastomer matrix confined in between filler particles. We have developed a mesoscale modelling of reinforced elastomers in which this local glass transition temperature shift is implemented. The model gives a unified picture and a semi-quantitative description of the whole set of complex mechanical phenomena observed in reinforced rubbers, in both the linear and nonlinear regimes: reinforcement over a large temperature range, drop of the modulus as amplitude increases (Payne effect), complex non-linear behaviour in Large Amplitude Oscillatory Shear.


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Tailor made and highly pure oligomers are required for biomedical applications. Since several years Solvay is a supplier of a very special fluorinated diol successfully used by CIBA VISION for a new generation of soft contact lenses (Night&Day®), so generating a very profitable business for our Company. A proprietary purification technique has been developed to match the severe specification requirements. It guarantees, trough and adsorption/desorption process onto silica gel, an average functionality > 1.99. This research reports a deeper investigation of the equilibrium of the adsorption/desorption of -CF2CH2OH terminated fluorinated oligomers onto this porous solid phase. Specifically, the molecules that have been evaluated belong to the class of functional PerFluoroPolyEthers (PFPEs), produced by Solvay Specialty Polymers. It has been demonstrated that the adsorption/desorption equilibrium of these PFPE reactive oligomers is quite well described by the classic Langmuir Model. More precisely, it has been determined that the affinity versus the solid phase (Silica Gel) parallels the number of functional groups per molecule, while the increase of the molecular weight, i.e. the length of the PFPE chain, exerts an opposite effect. As a consequence, these molecular parameters rule the entire adsorption/desorption phenomenon. However, some anomalies are observed during the desorption process when polyolic species are considered, such that an irreversible adsorption of these fluorinated oligomers appears just as effective. The hypothesis that an over-aggregation is promoted, when oligomers confined inside the pores are considered, seems adequate to describe this apparent irreversibility of the adsorption of polyfunctional oligomers. When this phenomenon is active the equilibrium process is completely hindered because the solvent isn’t able to disrupt these very stable aggregates that remain as confined species inside the silica pores any more. Consistently, mono-functional species that can form only smaller aggregates behave as expected on the basis of the classic Langmuir model. The hypothesis that the nano-confinement inside the silica pores promotes a super-aggregation with a dynamic formation of PFPE clusters much larger than expected simply on the basis of concentration is supported by several model calculations and studies. These results show that confinement can enhance the tendency to self-associate by as much as several orders of magnitude, especially when aggregates can adapt their shape to the shape of the rigid barriers of the confinement. This seems to be exactly the case of these very flexible fluorinated oligomers.
Glassy dynamics of densely packed semi-isolated polymer chains

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The glassy dynamics of randomly distributed, condensed isolated and semi-isolated polymer chains is studied by means of Broadband Dielectric Spectroscopy (BDS), poly(2-vinylpyridine) (P2VP) being the probe material. For this purpose, a recently developed nano-structured electrode arrangement is refined to achieve a miniature electrode-to-electrode separation of 35 nm. This geometry presents a pioneering opportunity to investigate both the structure (by Atomic Force Microscopy (AFM)) and the dynamics (via BDS) of exactly the same sample. Herein, the former technique reveals that the mean volume of the coils is 1 to 2 times the volume expected for a single chain, while the latter experiments demonstrate that (i) even single polymer chains exhibit VFT temperature dependence, being the characteristic feature for the dynamic glass transition; (ii) for P2VP coils on silicon, the mean relaxation time is bulk-like; and (iii) the relaxation time distribution is broadened especially in the low frequency range – a finding which we assign to interactions between the solid substrate and the first layer of chain segments in the direct vicinity of the interface.
The density profile of a polymer confined to a channel

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Biological polymers are usually found in confined environments, and the conformations and function of the polymers are fundamentally influenced by confinement [1]. In particular, a reduction in entropy causes the monomer density to decrease close to a wall. For an ideal chain, it is well known that the resulting density profile can be determined by the solution of a diffusion equation, with absorbing boundary conditions at the walls [2]. For a self-avoiding chain, the theory must be modified to account for the fact that the probability of collisions is similarly lowered in the vicinity of a wall. This effect can be included by adding the collision probability as a position dependent annihilation term in the diffusion equation. To bring closure to the equation, this collision probability must in turn be related to the solution of the resulting diffusion-annihilation equation. The conventional way of achieving closure is by assuming that the collision probability is proportional to the local monomer concentration of a long polymer, resulting in a self-consistent mean field theory [3].

The self-consistent theory neglects spatial correlations between monomers, and can thus be expected to describe the density profile of a semi-dilute solution of polymers, with frequent inter-chain collisions. However, in recent years there have been a number of experiments performed on single polymers confined to channels (see e.g. [4, 5]). It is thus necessary to revisit the question of the relation between the density profile and the collision probability for this system. We have studied the density profile and collision probability of a freely jointed chain by Monte Carlo simulations, and find that the relation does not agree with the assumption of the self-consistent theory. We show instead that the collision probability can be qualitatively explained by analysing the self-avoiding chain as a diffusing particle, with a drift velocity in the channel direction [6]. We find that most collisions occur between closely neighbouring monomers and that the collision probability is significantly higher than predicted by a mean-field theory, but does not depend as strongly on position.

Our results for the collision probability imply that the effect of self-avoidance on the density profile of a single polymer confined to a channel is weaker than predicted by the self-consistent field theory. We have tested this conclusion by Monte Carlo simulations of self-avoiding chains, and by showing that knowledge of the collision probability allows one to compute the density profile.

References:
Vibrational Dynamics and Mechanical Behaviors of Disordered Colloidal Packings

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In recent papers our group has experimentally studied the phonon modes [1,2] of disordered colloidal packings, and the role played by particular low-frequency quasi-localized phonon modes (“soft spots”) in driving particles to rearrange in response to compressive stress [3]; in addition we have studied the evolution of rearranging clusters or dynamic heterogeneity as a function of interparticle interaction [4] and aging [5] in colloidal glasses. I will describe more recent work which continues to explore the connections between dynamics of individual particles and mechanical response of disordered media.

Specifically, we employ colloidal suspension consists of temperature-sensitive hydrogel particles, poly(N-isopropyl acrylamide) (PNIPAM). The size-changing behavior of PNIPAM particles permits us to vary the colloid packing fraction simply by changing the temperature. Using video microscopy and particle tracking techniques, we derive vibrational modes from particle displacements, and we record particle rearrangements. We study correlations between the modes and the particle rearrangements due to laser-tweezer and thermally induced stresses, as well as in thermal equilibrium. The phonon modes reflect the energy barriers of local constraints, and the low-frequency quasi-localized phonon modes are believed to be related to the low energy barriers for particle rearrangements. As part of this investigation we have investigated some new variables, e.g., local strain field fluctuations caused by thermal motions. To study these phenomena, we derive the best-fit affine strain tensor and non-affinity [6] for each particle by analyzing the variations of local configurations around each particle. The spatial and temporal distributions of this local deformation permit us to probe the mechanical properties of our colloidal systems. We study how these mechanical properties evolve as the systems approaches the jamming transition. The local strain analysis provides a more direct link between local dynamics and global mechanical response. Finally, we describe how our work on the disordered colloidal packings might shed light on the mechanical behaviors of atomic and molecular glasses.

This work was carried out in collaboration with Tim Still, Ke Chen, Matthew Gratale, and Arjun G. Yodh from University of Pennsylvania, and Kevin Aptowicz from West Chester University.

References:
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